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PHYSICAL REVIEW

THE POSITION AND STRUCTURE OF THE MODIFIED LINE OF THE SPECTRUM OF SCATTERED X-RAYS

By F. L. Nutting

Ryerson Physical Laboratory, University of Chicago

(Received August 22, 1930)

Abstract

Measurements have been made by both photographic and single-crystal ionization methods of the shift in wave-length of scattered x-rays at angle of about 170°. The photographic method was that introduced by Sharp, but the $K\beta$ line of molybdenum was used. Two exposures of several hundred hours each were obtained. Analyses of the microphotographic records gave, from the shift of the center of gravity of the lines, $h/mc = 0.02305$A, and from the shift of the peaks, $h/mc = 0.2374$A. From the difference between different exposures, it is suspected that some hidden source of error is present, perhaps due to the effect of the $K\gamma$ line. Some 600 ionization curves give as an average $h/cm = 0.0240 \pm 0.00024$A. These results, compared with those of other experimenters, fail to indicate any definite departure from the theoretical value of $h/mc = 0.2422$A. This does not support the findings of Davis and Purks, who report a value of 0.022A. The form of the spectral lines observed seems inconsistent with a fine structure of the modified line such as reported by Davis and Purks. The modified line is however found to have a considerable natural breadth.

THE well-known expression given by A. H. Compton for the change of wave-length of x-rays scattered at any angle,

$$\delta\lambda = \frac{h}{mc}(1 - \cos\phi), \tag{1}$$

has been tested by many experimenters.[2] Though the results of most of these investigations have been in close agreement with the theoretical formula, recent studies by Davis and Purks and by Davis and Mitchell have appeared to show a wave-length change considerably smaller than the predicted value. It has therefore seemed worth while to try some new experiments of a precision type to measure the wave-length change. Both photographic and ionization methods were employed.

[1] A. H. Compton, Phys. Rev. **21,** 207 and 483 (1923).

[2] E.g. A. H. Compton, Phys. Rev. **22,** 409 (1923); P. A. Ross, Proc. Nat'l Acad. **10,** 304 (1924); H. M. Sharp, Phys. Rev. **26,** 691 (1925); Kallmann and Mark, Naturwissenschaften **14,** 3 (1925); Davis and Mitchell, Phys. Rev. **32,** 331 (1928); J. W. M. DuMond, Phys. Rev. **33,** 643 (1929); Davis and Purks, Phys. Rev. **34,** 1 (1929).

Photographic Method

The photographic method employed was in principle the same as that used by Sharp.[2] The apparatus consists of an x-ray tube with narrow glass walls and a thin glass window w (Fig. 1). The rays are scattered from a paraffin radiator R through an angle ϕ of almost 180°, and are reflected from a polished calcite crystal, through a 0.1 mm. slit S. The spectrum is recorded on a photographic plate P. This construction gives only small variations in the angle of scattering for rays coming from different parts of the scattering block.

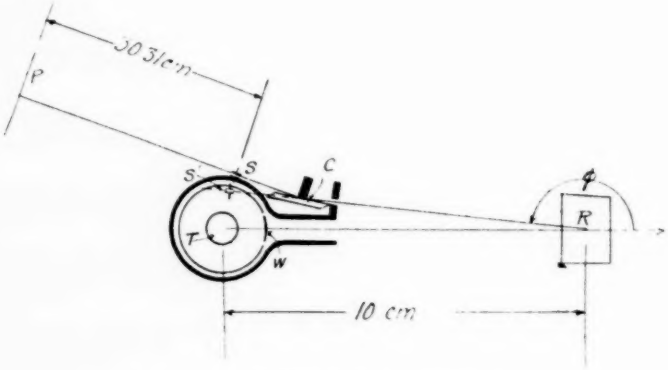

Fig. 1. Arrangement of apparatus.

In Sharp's experiments it was not possible to resolve the α doublet of the molybdenum rays which were used, and still retain sufficient intensity, and this incomplete resolution made necessary complicated corrections. In the present experiments, therefore, the measurements were made on the $K\beta$ line of molybdenum, which is a doublet so narrow that it may be treated as a single line.

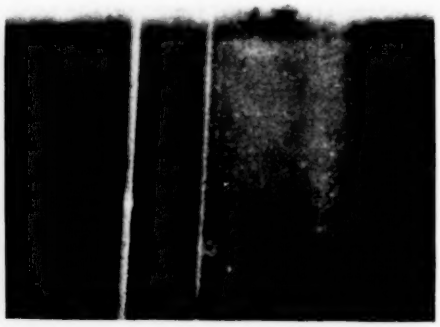

Fig. 2 Photograph of Mo K spectrum.

Two good exposures of several hundred hours were made, with the tube operating on a diffusion pump, at about 38 m.a. and 40 peak kv. To obtain standard reference lines, a molybdenum plate was placed in front of the paraffin radiator, and in some 50 hours a fluorescence spectrum of suitable

intensity was recorded without changing the position of the photographic film. Figure 2 shows one of the photographs thus obtained. The α_1, α_2, β and γ lines of the fluorescent spectrum are clearly visible, as well as the short wave-length continuous spectrum, the modified β line, and (faintly) the modified α line.

A microphotometric record of this film (the average of 11 curves on different parts of the spectral lines), taken with a Moll microphotometer, is shown in Fig. 3.

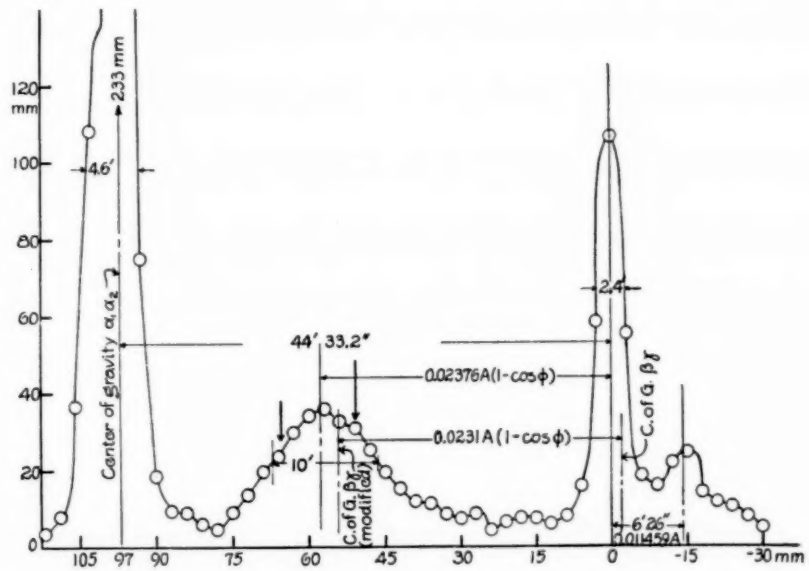

Fig. 3. Microphotometric analysis of Fig. 2. Mo K radiation; scatterers Mo plate and paraffin; $\phi = 169°$. Mean microphotometric curve.

Making use of Allison and Armstrong's value, for the wave-lengths of the molybdenum K lines, the mean of several measurements on the *center of gravity* of the modified $\beta\gamma$ line (cf. Fig. 3) give,

$$\delta\lambda = \lambda_{\beta\gamma}\text{mod} - \lambda_{\beta\gamma} = 0.045686A.$$

The mean value of $1-\cos\phi$ was found to be 1.9816, whence by Eq. (1),

$$h/mc = 0.02305A.$$

A similar measurement on the *peaks* of the β line and the β modified line, after correcting for the effect of the unresolved γ modified line in the manner described by Sharp,[2] gives

$$h/mc = 0.02374A.$$

For each individual film the consistency of the measurements was such as to indicate an error of about 1 percent. The results of the two films differed however by about 2.5 percent. This discrepancy suggests that there may be a hidden source of error, perhaps in the effect of the γ line on the position

of the modified peak which, would vary with the conditions of exposure and development. The measurement on the center of gravity depends upon the selection of a base line, and is thus less reliable than the measurement of the peak. It is doubtful therefore whether the observed difference between these results and the value $h/m=0.02422$A, calculated[3] from the accepted values of the constants, is of real significance.

Ionization Method

The values of h/mc obtained from these photographs depart from the accepted value of this quantity in the same direction though not as far as do the values obtained by Davis and his collaborators using the double crystal spectrometer. It was thought worth while therefore to repeat the measurement by an ionization method which should be free from the errors suspected in the photographic work.

In this method two Pyrex x-ray tubes with molybdenum targets were placed side by side, and a Soller[4] slit was used to increase the intensity of the modified radiation to be measured. Because of the low intensities of scattered radiation, an accurate determination of the position of the modified β line could not be made. The α doublet was therefore used, assuming in all calculations that $I_{\alpha_1}=2I_{\alpha_2}$, so that the common center of gravity would be 1/3 of their separation distance from α_1.

The experimental arrangement is shown in Fig. 4. To prevent melting

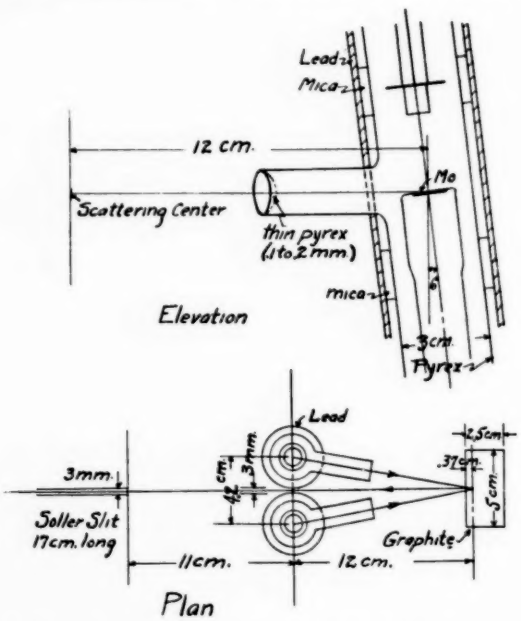

Fig. 4. Experimental arrangement for the ionization method.

[3] This is the average of the values 0.02417 and 0.02428 calculated by Birge (Rev. of Mod. Phys. 1, 64, 1929) from the spectroscopic and the deflection values of e/m respectively.

[4] W. Soller, Phys. Rev. **23**, 292 (1924).

of the waxed ground joint near the cathode of the x-ray tube, it was necessary to maintain a jet of compressed air on each tube. The tubes were operated continuously at 50 kv peak and about 30 m.a. each. The ionization chamber was sulphur insulated and filled with argon. A block of graphite was used as the scattering material. The angle measurements were made from a slow motion screw attached to a Bragg spectrometer. Calibration by a mirror, lamp and scale, showed the readings to be reliable to within 3 seconds over the range of angles used.

Some six hundred runs were made over both the modified and the unmodified lines, and the difference between the positions of their peaks noted. This gave

$$\delta\theta = 27' 11.6'',$$

whence, using $D_{\text{calcite}} = 3.029\text{A}$,

$$\delta\lambda = 0.04757A.$$

The mean scattering angle was 168° 39′, whence

$$(1 - \cos\phi) = 1.9804,$$

and by Eq. (1),

$$h/mc = 0.0240 \pm 0.00024A,$$

This result differs from the theoretical value of 0.02422A by less than the probable experimental error.

TABLE I. *Comparison of results.*

Author	Method	h/mc	Probable error per-cent	Deviation from theory percent
Theory	Accepted values of constants	0.02422	0.3	—
Kallmann and Mark	Mo K, photographic	0.0242	1.	0
Sharp	Mo K, photographic	0.02432	0.4	0.4
Davis and Purks	Mo K ionization double crystal	0.0221	—	−9.
Dumond[5]	Mo K Photographic	0.0234	—	−3.
Nutting[6]	Mo K, (Photographic (peak)	0.02374	1(?)	−2.
Nutting	Mo K ionization, single crystal	0.0240	1	−0.9
Gingrich[7]	Mo K ionization Double crystal	0.02424	0.2	0.1

[5] This is the writer's estimate from the data published by DuMond.
[6] The measurement on the center of gravity is not included for reasons given above.
[7] N. S. Gingrich, *Phys. Rev.* **36**, 364 (1930).
This result was published after the work here described was completed.

It will be seen that most of the experiments lie somewhat below the value required by theory. However, the deviation is smallest for the experiments that seem to be most reliable, and it thus appears doubtful whether the difference is a real one At least it can be said that the large deviation of the measurement of Davis and Purks is not confirmed by the other measure ments.

Structure of Lines

In the photographic method, there was a maximum spread of the modified line of 2.86 percent due to scattering angle variation. As is shown in Fig. 3, the modified line is not symmetrical, the long wave-length side being steeper. If we assume the same three principal components of the β modified line (neglecting γ of 1/7.7 the intensity) as those given by Davis and Purks[2] for the α_1 line, they would have produced a high peak at the position indicated in Figure 3 by the long arrow and a much weaker one further out (shorter arrow). There is a mere suggeston only of such components in the curve. There seems to be no way in which sharply defined components such as those reported by Davis and Purks could form a curve like the one found in these experiments.

An examination of Figure 2 shows that the resolving power of the spectrograph was sufficient to separate the lines of the α doublet of molybdenum, which are 0.0043A apart. The range of wave-lengths of the modified line due to the variation of 2.86 percent in $(1-\cos\phi)$ is 0.0007A, which is small in comparison with the apparent width of about 0.004A of the β line. This means that the variation in scattering angle results in no appreciable widening of the lines. The apparent broadening of the modified line as compared with the fluorescent lines must therefore mean a variation in wave-length of the rays scattered at a definite angle, in accord with the conclusion of previous observers.

AN EXPERIMENTAL STUDY OF THE RELATIVE INTENSITIES OF X-RAY LINES IN THE TANTALUM *L*-SPECTRUM

By Victor Hicks

University of California, Berkeley

(Received September 10, 1930)

Abstract

The relative intensities of 17 lines in the L spectrum of tantalum have been investigated by the ionization spectrometer. The following precautions were taken: (1) the rays were taken at a glancing angle of 45° from a polished tantalum surface; (2) a tantalum filament was used; (3) the slits were enclosed in an arm of the tube reducing the air path of the rays to 7.35 cm; (4) the coefficient of reflection of the crystal used was measured for the various wave-lengths by means of the double-spectrometer; (5) the absorption coefficients of the mica windows used were directly measured; (6) the rays were completely absorbed in methyl iodide vapor of known pressure; and (7) the slits were sufficiently wide to eliminate effects arising from the different natural widths of the lines. Measurements were taken at 30.6 kv and 20.7 kv and corrected to high voltage. The results for lines of small wave-length separation agree well with previous measurements of Allison and Armstrong and Jönsson on tungsten. For lines of larger wave-length separation ($L\alpha_1$, $L\beta_1$) the results of Jönsson are not confirmed, but the previous qualitative estimates of Allison and Armstrong are substantiated. The assumption that the ionization currents produced are proportional to the relative intensities is supported by recent work of A. H. Compton. If the ν^4 correction is made to the intensities at high voltage, the sum rules are approximately valid except for lines having initial state L_1. The intensity results are:

	l	α_2	α_1	η	β_4	β_1	β_3	β_2	β_7
Rel. Int. at 30.6 kv	1.5	10	100	1.3	9.3	93	13	40	0.8
Rel. Int. at high V.	1.5	10	100	1.4	11.	103	16	40	0.8
	$\beta_5+\beta_{10}$	β_9	γ_3	γ_1	γ_6	γ_2	γ_3	γ_4	
Rel. Int. at 30. 6 kv	1.1	0.8	1.2	29	0.6	5.0	7.2	2.2	
Rel. Int. at high V.			1.4	32	0.7	5.9	8.5	2.6	

Introduction

THE relative intensities of the lines in the tantalum L spectrum have been investigated with an ionization spectrometer, the method used being similar to that previously employed by Duane and Patterson,[1] Allison and Armstrong,[2] and Allison.[3] Considerable work has previously been done on the relative intensities in the tungsten L spectrum (atomic number 74). Duane and Patterson investigated the relative intensities of lines in the α, β, and γ groups, the members of which do not differ greatly in wave-length. They did not attempt to compare intensities of lines in different groups. Allison and Armstrong repeated and extended this work, and in addition made some qualitative estimates of the relative intensities of the more intense

[1] Duane and Patterson, Proc. Nat. Acad. Sci. **6,** 518 (1920) **8,** 85 (1922).

[2] Allison and Armstrong Phys. Rev. **26,** 714 (1925).

[3] S. K. Allison, Phys. Rev. **30,** 245 (1927), **32,** 1 (1928).

lines in the various groups, thus linking them together. Jönsson[4] investigated the relative intensities in the L series of tungsten, using a Geiger counter, and gave results for all the lines in the L spectrum. Within the α, β, and γ groups, where wave-length differences are small, the results of Allison and Armstrong and Jönsson were in fair agreement, but for lines of wider wave-length separation (i.e. those separated by the $L_{II}L_{III}$ frequency difference) there were large discrepancies. For instance, Allison and Armstrong reported that $L\beta_1(M_{IV}L_{II})$ was slightly more intense than $L\alpha_1(M_VL_{III})$ whereas Jönsson found the intensity ratio of α_1/β_1 to be 100/51.8. He ascribed this lack of agreement to the fact that there was more absorption in the target in the experiments of Allison and Armstrong than in his; this explanation seemed quite reasonable, because they had obtained evidence of the L critical absorption discontinuities of the target in their general radiation spectrum.

The present experiments on tantalum (atomic number 73) were undertaken in order to add to our knowledge of the L-series intensities in general, and to investigate the cause of the discrepancies mentioned above in particular. They show that Jönsson's explanation of the differences cannot be correct.

Apparatus

(1) *Power supply.* The high voltage direct current generating apparatus was that used by S. K. Allison for his measurements on the L-series of uranium.[3] The potential difference applied to the x-ray tube was measured with an electrostatic voltmeter, consisting of a dumbbell hung on a bifilar suspension between two parallel plates, the whole being enclosed in a grounded metal case. A lens system formed an image of an incandescent lamp filament on a ground glass scale at a distance of 3.8 meters from a mirror mounted on the vertical axis of the dumbbell. The voltmeter was calibrated in the following manner: the crystal table angle corresponding to the K absorption limit of molybdenum was first carefully determined by observing the reflected intensities while moving the crystal through small angular steps with a thin molybdenum sheet in the path of the beam. The crystal was then set at the proper position to reflect the wave-length corresponding to this absorption limit, and the sheet of molybdenum removed. The limiting voltage to excite this wave-length was then determined by lowering the voltage in steps until no reflected intensities were observed. Three other points were taken on the calibration curve by the use of thin sheets of silver, tin, and cadmium.

The experiments were performed largely at 30.6 kv, although some measurements were taken at 20.7 kv. With two condensers in series in the high potential circuits, each of 0.050 mf capacity, the calculated fluctuation in the high voltage at 30.6 kv was 0.4 percent when a tube current of 3 ma was used. It was found convenient to operate the tube with the cathode grounded through the milliammeter.

(2) *X-ray tube.* The x-ray tube, the glass parts of which were constructed of Pyrex, is shown in Fig. 1. The most important features of this tube were:

[4] A. Jönsson Zeits. f. Physik **36**, 426 (1926).

(1) The slits were built into the tube as an integral part, thus cutting down the path of the rays in air; (2) the orientation of the cathode stream with respect to the axis of the tube could be changed while the tube was evacuated, thus permitting the focal spot to be brought opposite the slits. The slits were of iron, mounted on a tube of iron enclosed in a glass arm of the x-ray tube. The width of the slits was 0.18 mm, the height 1.6 cm, and the distance between the slits was 40.0 cm. This limited the horizontal angular width of the beam to approximately 3 minutes of arc. The x-ray beam left the tube through a mica window in a brass cap on the arm carrying the slits. As the slit system was fixed with reference to the anode, it was necessary to adjust

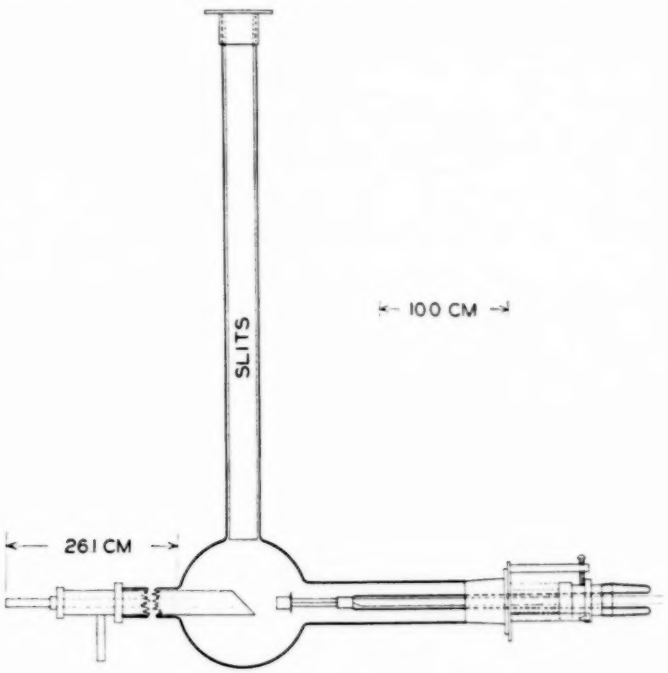

Fig. 1. Diagram of x-ray tube.

the position of the focal spot on the anode. This was accomplished by having a section of the arm of the tube carrying the cathode made of flexible silphon copper tubing. The orientation of the cathode beam with respect to the axis of the tube could then be changed by set screws, two of which are indicated in Fig. 1.

The anode was made of copper. A piece of sheet tantalum and a spool of tantalum wire 0.025 cm in diameter for filaments were given us by the Fansteel Products Co. The tantalum was 99% pure. The tantalum was spot-welded to a piece of nickel, and then the nickel soldered to the anode. With the tantalum spot-welded in about twenty points, no local heating was experienced at the low tube currents used, and the target was not pitted at the close of the experiments.

The anode was cooled by pumping kerosene through it. This prevented any electrical conduction to ground which might have taken place if water were used for cooling.

The x-ray tube was exhausted continuously while being operated. The tube and the glass part of the vacuum system were mounted on a stand which permitted translation, rotation, and leveling of the tube.

(3) *Spectrometer.* The spectrometer was of the Bragg type. Angular settings of the crystal were read with microscopes on an accurately divided circle 25.4 cm in diameter; settings could be made to 15 seconds of arc with ease, more precise settings were not necessary in this work. The axis of the spectrometer was 48 cm from the focal spot of the x-ray tube.

(4) *Ionization chamber.* The ionization chamber was of the type described by Williams and Allison.[5] It was made of a Pyrex glass tube 4.7 cm in internal diameter and 33 cm long. To one end were attached the tubing and valves for introducing the gas and a ground glass joint for an iron guard ring. An amber plug supporting a nickel rod fitted tightly into the guard ring. The nickel rod was connected to the electrometer by very carefully shielded wires. Just inside the inner wall a cylinder of nickel gauze was placed as the charged electrode. The length of the gauze was 28 cm, and the nickel rod was 1.4 cm from the nearest point of the gauze. The end of the chamber towards the crystal was closed with a brass cap having a slit 0.3 cm wide by 2.9 cm high, over which a piece of mica was sealed with deKhotinsky cement. The effective angular width of this slit at the axis of the spectrometer was about 4°, so that it was not necessary to move the ionization chamber frequently when taking readings. A potential of 170 volts supplied to the nickel gauze by means of a dry battery was sufficient to insure saturation currents through the gas in the chamber, since frequent trials during the measurements showed that the rate of deflection of the electrometer was proportional to the electron current in the x-ray tube. Methyl iodide was used as the absorbing gas. A clear colorless liquid was obtained by stirring the methyl iodide with granulated zinc to remove any traces of free iodine. The liquid was then filtered into a small bulb, frozen by immersion in liquid air and the bulb sealed to the ionization chamber through a stopcock. The ionization chamber was then evacuated, keeping the methyl iodide immersed in liquid air, and the methyl iodide vapor introduced into the chamber through phosphorus pentoxide by allowing the liquid to warm up to room temperature gradually. Air was finally introduced over phosphorus pentoxide to bring the vapor in the chamber to atmospheric pressure.

(5) *Electrometer.* The electrometer was a Compton type used heterostatically. The currents were measured by observing the time rate of charging of the insulated pair of quadrants. A sensitivity of about 1800 scale divisions per volt with a mirror to scale distance of 1.75 meters was sufficient for the majority of the measurements.

[5] Williams and Allison, J. Opt. Soc. Am. and Rev. Sci. Inst. **18,** 473 (1929).

Method of Measuring Intensities

A fundamental assumption in this method of measuring relative intensities is that the observed ionization currents are proportional to the intensities of the x-ray beams entering the ionization chamber, even when these beams differ in wave-length. This assumption will be discussed later. At present the method of obtaining what may with strict accuracy be called the relative ionization currents from the observed electrometer readings will be described. These were taken as proportional to the height of the tip of the peak representing the line above the base-line of scattered and general radiation. This method is justified if the following conditions hold true: (1) the curve representing each line must be symmetrical about the center of the line; (2) the resolution must be great enough so that the radiation due to a line is negligible at a distance from the center of the line equal to twice the wave-length separation from the nearest line; (3) the resolution must not be so great that the natural breadths of the lines play any part in the curve representing the line. Allison[6] has found that in the iridium L spectrum the line $L\beta_2$ has an angular width at half-maximum corresponding to a range of reflection of about 45 seconds of arc from a single crystal of calcite in the first order. The angular width of the beam was 3 minutes of arc, and all the lines measured had the same full width at half-maximum, namely 2′30″, so it is seen that assumption (3) was fulfilled. The angular width of the beam was not so great, however, as to violate the second assumption. For instance, the base-line for $L\alpha_1$, according to this method, is taken at an angle corresponding to $\lambda_{\alpha_2}+\Delta\lambda$, where $\Delta\lambda$ is the wave-length separation of α_1 and α_2. By the symmetry of the lines, the radiation at this point is the fraction of α_2 appearing under α_1 plus baseline currents. The intensity at this point, however, was found to be very little different from that of the base-line farther away in agreement with condition (2).

Corrections to be Applied to Observed Readings

Corrections to be applied to observed values arise from the following: (1) absorption of the rays in the target of the tube, (2) absorption in the mica windows in the tube and ionization chamber, (3) absorption by the air traversed by the beam, (4) incomplete reflection by the calcite crystal, (5) partial absorption in the ionization chamber. In computing the corrections for these factors ((4) excepted) the mass absorption coefficients of the materials were assumed to vary with the cube of the wave-length throughout the tantalum L spectrum. If μ is the absorption coefficient of the material for the line $L\alpha_1$, μ' that for another line, and t the thickness of the material, the correction to be applied to the intensity of the line relative to that of α_1 is

$$e^{-(\mu-\mu')t}$$

(1) The radiation used in the experiments was taken at an angle of 45° from the target face so that the thickness of the target traversed was the same for the impinging electrons and the emerging x-rays. No evidence of the L_{II} or L_{III} absorption discontinuities in the general radiation spectrum

[6] S. K. Allison, Phys. Rev. **34**, 176 (1929).

was found, as in the previous work of Allison and Armstrong on tungsten. The extent of the correction to be applied for this effect is probably less than 5 percent and is rather uncertain,[7] so that no such correction has been applied here.

Further, since a tantalum filament was used throughout the experimental work, no foreign substance could have been deposited on the face of the target. This eliminates a doubtful correction which may enter when the target and filament are not of the same substance.

(2) The absorption coefficients of the mica used for windows were found by direct measurement to be 138 for Ta $L\alpha_1$, 93.5 for Ta $L\beta_1$ and 60.4 for Ta $L\gamma_1$. These values are approximately proportional to the cube of the wave-length, as expected. The total thickness of mica in the path of the beam was 0.0053 cm.

(3) Due to the fact that the slit system was a part of the x-ray tube, and therefore evacuated, the distance travelled by the x-rays in air was only 7.35 cm. From the values of μ/ρ for air listed in the International Critical Tables[8] a mean value of 8.65 was computed for the mass absorption coefficient of air for the wave-length corresponding to $L\alpha_1$ of tantalum. The values of μ/ρ for the other lines in the spectrum were obtained from this value by assuming a variation proportional to λ^3.

(4) The final measurments of the relative intensities of the lines $L\alpha_1$, $L\beta_1$ and $L\gamma_1$ which were used to link together the intensities in the α, β, γ groups were made with a crystal whose reflection coefficients for these wave-lengths were directly measured by the method of Davis and Terrill.[9] The double spectrometer constructed in this laboratory and described by Williams and Allison[5] was used, with a tungsten target tube. The voltage used was sufficiently low to prevent second order reflections at the angles concerned. The reflection coefficients per degree for the $L\alpha_1$, $L\beta_1$ and $L\gamma_1$ lines of tungsten were found to be 0.00208, 0.00222, and 0.00232 respectively. The corresponding wave-lengths in X.U. are 1473.5, 1279.2, 1095.5. The correction to be applied to the tantalum spectrum was computed from these values.

[7] The measurements of Backhurst (Phil. Mag. **7**, 353 (1929)) on the absorption coefficients of platinum and gold through the region of their L absorption discontinuities has made it possible to calculate these corrections to the platinum L spectrum, assuming that the penetration of the electrons in the target is roughly given by the Thompson-Whiddington law. The critical L series ionization potentials of platinum average about 13kv. Using values of the constant in the Thompson-Whiddington law from the paper of Terrill (Phys. Rev. **22**, 101 (1923)) it is found that 34 kv electrons incident will penetrate 1.1×10^{-4} cm before their velocity is reduced to 13 kv. The depth of penetration of a large majority of the electrons is considerably less than this, due to the curving paths, and furthermore the classical theory predicts that they are most efficient in ionizing when their energy is twice that of the level to be ionized, that is, 26 kv electrons are most efficient in excitation of the platinum atom to the L state. If then we assume that the effective absorbing layer is half that above, and use Backhurst's absorption coefficients, we find that the largest correction to be applied in the L spectrum is a 5 percent reduction in $L\beta_1$ with respect to $L\alpha_1$.

[8] International Critical Tables vol. VI, p. 16.

[9] Davis and Terrill, Phil. Mag. **44**, 463 (1923).

(5) The International Critical Tables[8] list four mass absorption coefficients for methyl iodide corresponding to wave-lengths in the tantalum L spectrum. From these, a mean of 251 was computed for this coefficient for Ta $L\alpha_1$. The vapor pressure of the methyl iodide in the ionization chamber was 24 cm, the temperature, 20°C. This corresponds to a density of 2.17×10^{-3} gm/cm.^{3} Neglecting the absorption of the air introduced into the chamber, these data indicate that 99.9 percent of the line of shortest wave-length, γ_4, was absorbed in the chamber. It is thus evident that no correction need be applied for the relative absorption in the ionization chamber.

Results

The principal results of the investigation are shown in Table I, which gives the results of measurements taken at 30.7 kv. In column 6 of this table a factor is given by which the intensities at high voltage can be calculated. The intensities calculated by this factor would not take account of absorption in the target which might become more pronounced at high voltage. In making this calculation it was assumed that the variation of intensity with voltage of a line can be represented by

$$I_v = C(V - V_0)^{1.8}. \tag{2}$$

The exponent 1.8 was chosen, not from any independent determination of the variation of the intensity of lines in the tantalum L spectrum with voltage, but from the previous values of Jönsson[4] who found 1.7 for tungsten, and Allison[3] who found 1.8 for uranium. The voltage corrections to be applied to the tantalum L spectrum at 30.6 kv are small and the difference between the corrections computed with exponents 1.8 or 1.7 would be negligible.

Table I. *Relative intensities of lines in the tantalum L spectrum from ionization measurements at 30.6 kv.*

Line	Wave-length X.U.	Obs. Rel. intensity	Corr. factor for absorption	Rel. Int. 30.6 kv.	Factor to give rel. int. at high voltage	Rel. int. at high voltage.
l	1724	1.0	1.43	1.5	1.00	1.5
α_2	1530	10	1.02	10	1.00	10
α_1	1519	100	1.00	100	1.00	100
η	1466	1.4	.91	1.3	1.11	1.4
β_4	1343	12	.77	9.3	1.18	11
β_1	1324	122	.76	93	1.11	103
β_3	1304	18	.74	13	1.18	16
β_2	1282	56	.72	40	1.00	40
β_7	1260	1.1	.71	0.8	1.00	0.8
$\beta_6+\beta_{10}$	1251	1.6	.70	1.1		(1.1)
β_9	1243	1.2	.69	0.8		(0.8)
γ_5	1170	1.9	.64	1.2	1.11	1.4
γ_1	1136	47	.62	29	1.11	32
γ_6	1110	1.1	.60	0.6	1.11	0.7
γ_2	1103	8.3	.60	5.0	1.18	5.9
γ_3	1097	12	.60	7.2	1.18	8.5
γ_4	1062	3.8	.58	2.2	1.18	2.6

The observed relative intensity of $\alpha_1:\beta_1:\gamma_1$, listed as 100:122:47 in column 3 of Table I has already been corrected for the measured coefficient of reflection of the calcite crystal used. The values observed without this correction were 100:128:52. Each value given in column 3 of Table I is the result of at least four independent measurements, which were averaged.

In the β group of lines, β_1 and β_6 could not be separated in the first order because of the wide slits used. Previous measurements with tungsten[2,4] indicate that β_6 is about 2 percent as strong as β_1; thus a large error in the measurement of β_1 could not be made by the inclusion of β_6 under part of the curve. β_5 and the non-diagram line β_{10} have the same wave-lengths in tantalum; the sum of their intensities is given in the table, but not corrected to high voltage. No attempt was made to separate the very weak line β_8 from β_2.

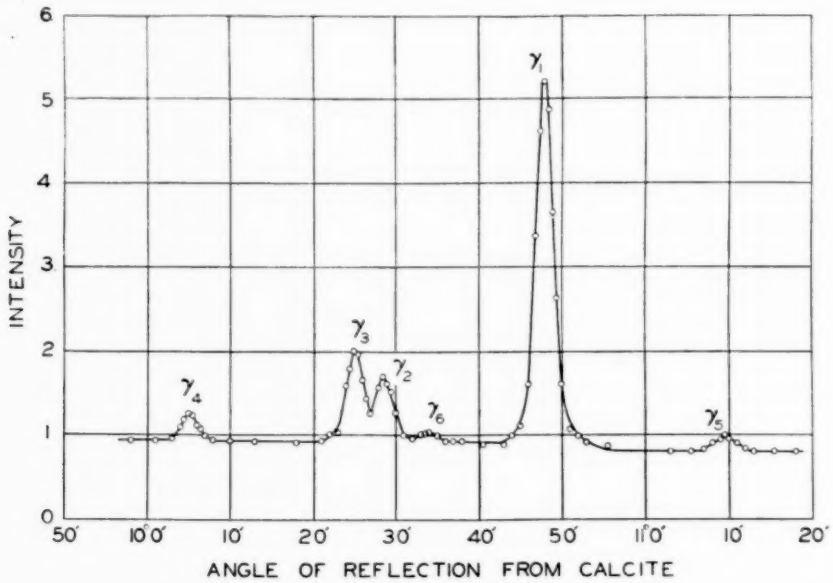

Fig. 2. Tantalum L spectrum, γ group.

In the γ group intensity measurements were made on all the lines listed by Lindh[10] for tantalum. A typical ionization spectrum of the $L\gamma$ group is shown as Fig. 2.

Discussion of the Experimental Method

Mention has previously been made in this paper of the grouping of the L-series lines (except the weak lines l and η) in three regions of small wave-length range compared to that of the spectrum as a whole. This fact makes it convenient to divide the problem of determining the relative intensities of the lines into two problems: (1) finding the relative intensities of the lines in a single group; (2) comparing the intensities of lines in different groups. The first of these problems seems to be comparatively simple. All investiga-

[10] A. E. Lindh—Handb. der Experimentalphysik XXIV 2 Teil, p. 154 (1930).

tors have found the relative intensities of α_1/α_2 to be 100/10 or 100/11. Table II shows the results of three different investigations in the β and γ groups of the adjacent elements, tantalum and tungsten. The results of Allison and Armstrong quoted in Table II are the results originally in their paper multiplied by the appropriate high voltage factor to bring them to the same basis as the others.

TABLE II. *Relative intensities of lines in groups of small wave-length separation.*

Line	$L\beta$ group. Ta (73) Hicks	W (74) Allison and Armstrong	W (74) Jönsson	Line	$L\gamma$ group Ta (73) Hicks	W (74) Allison and Armstrong	W (74) Jönsson
β_1	(100)	(100)	(100)	γ_1	(100)	(100)	(100)
β_2	39	43	39	γ_2	18	15	16
β_3	16	16	16	γ_3	27	24	22
β_4	11	8.2	10	γ_4	8.1	7.5	6.5
β_5		.41	.39	γ_5	4.4	3.0	4.5
β_6		1.8	1.9	γ_6	2.2	2.3	3.3

In the measurement of the relative intensities of the lines $\alpha_1:\beta_1:\gamma_1$, representative of the α, β, and γ groups respectively, much larger differences between the measurements of Jönsson and the ionization chamber measurements are found. This is illustrated in Table III. It is evident that when larger wave-length separations are involved, much lower intensities for the

TABLE III.

Line	Ta (73) Hicks	W (74) Allison and Armstrong	W (74) Jönsson
α_1	(100)		(100)
β_1	103	"slightly more intense than α_1"	51.8
γ_1	32	"more than $\frac{1}{2}$ as intense as β_2"	9.1

shorter wave-length lines were obtained with the Geiger counter (Jönsson) than with the methyl iodide ionization chamber. The differences cannot be due to a sudden change in relative intensities between the elements tantalum and tungsten. In preliminary trials in these experiments a tungsten target was used and it was found that β_1 was somewhat more intense than α_1, as previously reported by Allison and Armstrong, although quantitative measurements were not carried out on tungsten in the present research. In a later paper Jönsson has himself pointed out[11] that in the sensitive region near the point in the counter only a small fraction of the radiation is absorbed, and from the known absorption coefficients this fraction must vary with the wave-length of the line. Although Jönsson corrected his observations in the L series of the elements of atomic numbers 42–47 for this partial absorption, he did not apply this correction to his results on tungsten and platinum.

[11] Jönsson, Zeits f. Physik **46**, 383 (1928).

If this correction is applied to his results as given in column 4 Table III, values somewhat nearer those in column 2 are obtained. The remaining discrepancy may be due to the photo-electron range which in air is great enough to allow the ejected electrons to escape from the sensitive region near the point without producing their full quota of ions.

In the present research an experiment was performed to demonstrate the effect of this partial absorption in the detecting device. The methyl iodide vapor was pumped out of the ionization chamber and dry air admitted to a pressure of 15 cm. In a chamber 28 cm long this gives the same mass of air in the path of the x-ray beam as in Jönsson's experiments where a chamber 5.5 cm long was used at atmospheric pressure. Ionization measurements of $\alpha_1:\beta_1:\gamma_1$ were carried out in this air-filled chamber, and all corrections for absorption outside the chamber were made. The resulting "intensities" at high voltage were 100:43:5.7, which is of the order of Jönsson's results as quoted in column 4 of Table III. It must therefore be concluded that Jönsson's results in tungsten and platinum for lines of different groups are seriously in error due to neglect of this partial absorption factor.

Another difference between Jönsson's method of measuring and the one reported here is that his measurements were taken at 20 kv and extrapolated to high voltage, whereas the present measurements were taken at 30.6 kv and extrapolated. In order to find out if part of the differences between these results and his were due to this cause, a number of observations were made on the relative intensities of $\alpha_1:\beta_1:\gamma_1$ at 20.7 kv. These are listed in Table IV.

TABLE IV. *The ratios $\alpha_1:\beta_1:\gamma_1$ from measurements at 20.7 kv.*

Line	Observed rel. int.	Corr. factor for absorp.	Rel. Int. 20.7 kv.	Voltage Corr.	Rel. Int. high voltage
α_1	(100)	1.00	(100)	1.00	(100)
β_1	112	.76	85	1.24	105
γ_1	46	.62	28	1.24	35

The "observed relative intensities" given in column 2 of this table have already been corrected for the variation of the coefficient of reflection of the crystal with wave-length. From a comparison of Table IV and Table I it is apparent that measurements taken at 20.7 kv give approximately the same values as those taken at 30.6 kv when extrapolated to high voltage.

The method of measuring relative intensities used here has received considerable support from recent work by A. H. Compton.[12] Compton has shown that unless the saturation currents obtained in his ionization chamber (corrected for the fraction of the beam absorbed in the chamber, and the fraction of the fluorescent radiation produced in the chamber which escaped to the walls without production of photo-electrons in the gas) were proportional to intensities, the efficiency of production of fluorescent radiation for a given atom would be found to vary with the wave-length of the primary radiation. Compton states that his experiments support the conclusion that the ioniza-

[12] A. H. Compton, Phil. Mag. **8**, 961 (1929).

tion by β-rays per unit energy is independent of their energy. Such conclusions had already been reached by Kulenkampff,[13] Kircher and Schmitz[14] and Crowther and Bond,[15] but the experimental arrangement used by Compton was more like that used in these experiments in that he used an ordinary methyl bromide filled chamber rather than air. In the present experiments, the tantalum radiations entering the ionization chamber were never sufficiently hard to excite the K series of the iodine; only the relatively soft L series of wave-length around 2.8A could be emitted. From the dimensions of the chamber it may be calculated that only a negligible fraction of this iodine fluorescent radiation could reach the walls without expending itself in the production of photo-electrons. Furthermore, the range of the photo-electrons ejected by the tantalum L series wave-lengths from the iodine atoms was not over 2.5 mm as can be calculated from the Thompson-Widdington law. Therefore no photo-electrons could have reached the walls of the chamber without producing their full quota of ions.

Discussion of Results

If it is conceded that the ionization method, as employed here and by Allison and Armstrong in tungsten, and Allison in thorium and uranium gives the correct relative intensities of the lines, the present results give the problem of the intensities of x-ray lines in the L-series an entirely new aspect. It is necessary to assume that the agreement between the measurements of Jönsson on tungsten (74) and those of Allison on thorium (90) and uranium (92) was fortuitous, and that the relative intensities in the L series undergo a large change in the region between atomic numbers 73 and 92. This is illustrated in Table V.

Table V. *Relative intensities at high voltage in the tantalum and uranium L-series*

	l	α_2	α_1	η	β_6	β_2	β_4	β_5	β_1	β_3	γ_5	γ_1	γ_2	γ_3	γ_6	γ_4
Ta(73) (Hicks)	1.5	10	100	1.4		40	11	<1.1	103	16	1.4	32	5.9	8.5	0.7	2.6
U(92) Allison	2.4	11	100	1.0	1.6	28	4.1	6.4	49	4.2	0	12	1.5	1.4	2.2	0

The development of the new quantum mechanics has made it increasingly evident that there is a factor in the expression for the intensities of spectral lines which is the fourth power of their frequency.[16] This ν^4 correction is to be applied to widely separated multiplets in optical spectra, and the intensities so corrected should be governed by the sum rules or their extension in case the Boltzmann factors are not appreciably different for the initial levels of the transition. In the L-series, instead of the Boltzmann factor, we have an ionization function, which gives the relative number of atoms in the target ionized in the L_I, L_{II}, L_{III} levels by the impinging electrons.

[13] H. Kulenkampff, Ann. d. Physik **79**, 97 (1926).

[14] Kircher and Schmitz, Zeits. f. Physik **36**, 484 (1926).

[15] Crowther and Bond, Phil. Mag. **6**, 401 (1928).

[16] For instance Pauling and Goudsmit: The Structure of Line Spectra, McGraw Hill (1930) pp. 128–143.

Allison[17] has pointed out that if the classical ionization function is taken, the relative intensity at high voltage of two lines having different initial states is very nearly equal to the ratio of the product of the transition probability by the statistical weight of the initial state. Since the transition probabilities involve ν^3 this suggests a ν^3 correction for lines involving different L sublevels. Table VI gives the observed and corrected intensities and comparison with sum rule values.

TABLE VI.

Lines		Experimental relative intensities.	Corrected for ν^4.	Corrected for ν^3 (for lines of different initial states)	Sum rules
$\alpha_1:\alpha_2:\beta_1$	Ta(73)	100:10:103	100:10:59	100:10:68	100·11:56
	U (92)	100:11:49	100:11:19	100:11:24	
$l:\eta$	Ta(73)	100:93	100:49	100:57	100:50
	U (92)	100:46	100:15	100:20	
$\beta_3:\beta_4$	Ta(73)	100:69	100:78		100:50
	U (92)	100:98	100:120		
$\beta_2:\gamma_1$	Ta(73)	100:80	100:49	100:56	100:50
	U (92)	100:43	100:19	100:23	
$\gamma_3:\gamma_2$	Ta(73)	100:69	100:71		100:50
	U (92)	100:107	100:112		

From Table VI it is seen that a ν^4 correction brings the relative intensities of lines in tantalum multiplets containing the large $L_{II}L_{III}$ separation surprisingly near the sum rule values. In uranium, on the other hand, the experimental results, uncorrected for frequency, are near the sum rule values, and if frequency corrections are made, wide departures from the rules are found.

In x-ray spectra, in contrast to optical spectra, there always exists the possibility of an internal radiationless transition, or Auger effect. If the probability of such an event taking place varies with the atomic number of the element, and is different for different L-series lines, an explanation of Table VI could perhaps be presented on this basis. So very little is known about the Auger effect for L-series lines, however, that at present, speculation seems futile.

It is indeed a p'easure to thank Professor S. K. Allison for the suggestion of this problem and for valuable assistance during the investigation.

[17] S. K. Allison, Phys. Rev. **32**, 1 (1928).

A STUDY OF THE VELOCITIES OF H^+ IONS FORMED IN HYDROGEN BY DISSOCIATION FOLLOWING ELECTRON IMPACT

By W. Wallace Lozier

Physical Laboratory, University of Minnesota

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Abstract

An apparatus is described which is suitable for a study of the velocity distribution of ions formed by single electron impact Electrons, confined to a narrow beam by a magnetic field, pass along the axis of two coaxial cylinders, ionize the gas, and are collected by a trap. The thick, inner cylinder, which is slotted, serves to allow only ions moving perpendicularly to the electron beam to pass to the outer collecting cylinder. A retarding voltage is applied between the cylinders. A study of the positive ion current collected as a function of the retarding voltage permits a determination of the velocity distribution of the ions. The above method is employed in a study of hydrogen.

Velocity distribution of H^+ ions formed by electron impact in H_2. Theory shows that when the H_2 molecule is ionized by electron impact, it may prove unstable and dissociate into $H^+ + H$ (or H′) or into $H^+ + H^+$ if two electrons have been removed. The H^+ ions thus formed possess kinetic energy. The H^+ ions coming from dissociation into $H^+ + H$ should occur at minimum electron velocities of about 27 to 40 volts, possessing roughly 5 to 11 volts velocity; while the H^+ ions resulting from removal of two electrons occur at minimum electron velocities of 46 to 56 volts, possessing 7.5 to 12.5 volts velocity. In agreement with the predictions of the theory it was found that the velocities of those ions resulting from dissociation into $H^+ + H$ and $H^+ + H^+$ together with the minimum velocities necessary to produce them satisfy linear relationships.

Introduction

As PREDICTED by Condon[1] and first experimentally verified by Bleakney and Tate[2] and Bleakney[3] the ions formed by electron impact in hydrogen will, in general, if molecular dissociation follows the ionization process, acquire kinetic energies corresponding to several electron-volts. The repulsive forces which are operative in the dissociation process and to which the ions owe their resultant kinetic energies are due, in case both electrons are removed from the H_2 molecule, to the ordinary classical repulsion of two protons. In the case of the removal of but one electron from the molecule, however, the repulsive forces between the proton and the neutral (or possibly excited) H atom are non-classical and find their interpretation in terms of the quantum mechanics.[4] For this reason a more precise experimental study of the energy distribution among the ions so formed than was

[1] E. U. Condon, Phys. Rev. **35**, 658 (1930) (Abstract).

[2] W. Bleakney and J. T. Tate, Phys. Rev. **35**, 658 (1930). (Abstract).

[3] W. Bleakney, Phys. Rev. **35**, 1180 (1930).

[4] Burrau, Kgl. Danske Vid. Selskal. Math-fys. Med. **7**, 14 (1927). P. M. Morse and E. C. G. Stueckelberg, Phys. Rev. **33**, 932 (1929).

possible with the experimental arrangement of Bleakney and Tate was deemed advisable and was undertaken at their suggestion.

Predictions of the Theory

The theoretical potential energy curves for the hydrogen molecule given by Bleakney from sources quoted in his article[3] are reproduced in Fig. 1. The ordinates of these curves represent the potential energies, in volts,

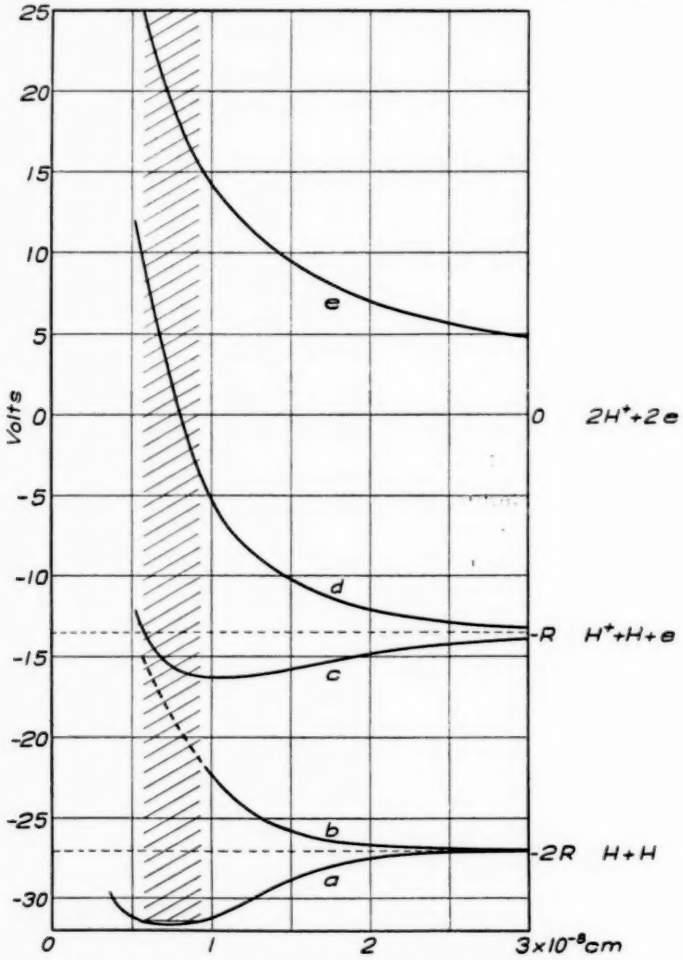

Fig. 1. Potential energy curves for the H_2 molecule.

of the various modes of bringing together the constituents of the hydrogen molecule as a function of the nuclear separation in Angstrom units. The zero of energy is taken with all of the constituents an infinite distance apart.

Curves *a* and *b* represent the two modes of bringing together two normal H atoms to form an H_2 molecule. The state *b* is unstable, while the state *a* represents the stable H_2 molecule. Curves *c* and *d* represent the two modes of bringing together a proton and a normal H atom to form the H_2^+ molecular ion. Curve *e* represents the one mode of bringing together two protons

to form an unstable H_2^{++} ion. The shaded area on the diagram represents approximately the range of separation of the two H atoms in the lowest vibration state of the H_2 molecule. It must be pointed out that this region is not entirely definite. The relative probability of finding the normal molecule with a given separation is greatest for the position of minimum potential energy and diminishes for separations greater or less than this. There is, however, some slight probability of finding the molecule with separations lying outside the shaded area.

The Franck-Condon principle states that transitions caused by electron impact, from the normal state to the states represented by the upper curves will be undergone without appreciable change in the nuclear separation. The molecule can be raised to the various states by an impacting electron possessing sufficient energy. Transitions to the state *b* would result in the dissociation of two normal atoms having from 3 to 6 volts kinetic energy. These have no significance for the present experiment, for the products would be uncharged. Transitions to state *c* would result in two possibilities. If the molecule be raised to any potential below -13.5 volts there would be formed stable H_2^+. However, for transitions to slightly higher potentials dissociation could result, giving H^+ and H possessing small amounts of kinetic energy. Only slight evidence for this transition was observed in the present experiment, however it has been observed by Bleakney[3] and has been suspected by others.[5] At minimum electron velocities of 27 to 40 volts, transitions to state *d* should be effected, resulting in dissociation into H^+ and H, each having velocities of 5 to 11 volts. With minimum electron velocities of 46 to 56 volts transitions to *e* should be possible, resulting in two H^+ ions having from 7.5 to 12.5 volts velocity. These are the transitions with which these experiments are concerned. The values given assume the transitions to take place within the shaded area. Since there is some probability of finding the molecule with separations beyond this region we would not expect the velocity distribution of the ions to terminate abruptly at the given values, but quite rapidly decrease beyond these.

In addition to these potential energy curves, there are a number of similar ones, not shown, corresponding to the removal of one electron from the H_2 molecule followed by dissociation into H^+ and H in its various excited states. In these experiments there was observed no evidence of transitions leading to dissociation into $H^+ + H'$. This leads one to suspect a relatively low probability for these processes.

Relations between energy of ions and energy of impacting electron. The electron velocity necessary to produce a given velocity ion from one of the states may well be called the ionization potential for the formation of an ion of that velocity from the specified state. If the initial energy of the molecule be E_1, that after dissociation E_2, the ionization potential V_i, and the kinetic energy of the ions V_F, then for the states *d* and *e*, or any similar ones,

[5] H. D. Smyth, Proc. Roy. Soc. **A105,** 116 (1924) and Phys. Rev. **25,** 452 (1925). T. R. Hogness and E. G. Lunn, Proc. Nat. Acad. Sci. **10,** 398 (1924) and Phys. Rev. **26,** 44 (1925).

$$V_i = (E_2 - E_1) + 2V_F. \tag{1}$$

This assumes; the dissociating entities possess equal kinetic energies, and no radiation takes place during the process of dissociation. For transitions to the state *d* this becomes

$$V_F = \tfrac{1}{2}V_i - \tfrac{1}{2}(31.4 - 13.5) \text{ (volts)} \tag{2}$$

While for transitions to the state *e*

$$V_F = \tfrac{1}{2}V_i - \tfrac{1}{2}(31.4 - 0). \tag{3}$$

These are the equations of straight lines with the slope one-half. Regardless of the shape of the potential energy curve for either of these states, the velocities of the ions and their ionization potentials must satisfy the relations above. The shape of the potential energy curves would, however, have an effect upon the form and range of the velocity distribution curve of the ions.

The Apparatus

The apparatus, shown in Fig. 2, was constructed of copper and was sealed in a Pyrex glass tube, which was then evacuated and baked out

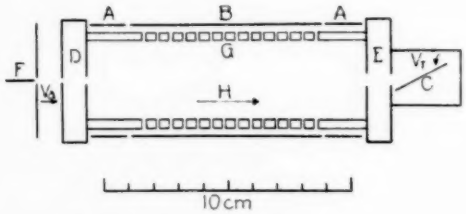

Fig. 2. Diagram of the apparatus.

several hours at 400° C. The source of electrons was a fine, sharply-pointed tungsten wire filament. An accelerating potential V_a was applied between the mid-point of the filament and the diaphragms *D*. The electrons passed through the holes in *D* and then through those in the diaphragms *E* and were finally collected at *C*. V_T was a potential of 175 volts holding the electrons to the plate *C*. A magnetic field *H* in the direction of the electron beam prevented any lateral spread. The electrons in traversing their path ionized the gas and ions were liberated, presumably in all directions. *G* was a circular cylinder with its axis along the electron beam. In it were cut a number of slots running around the circular boundary of the cylinder. These served to define the directions of the positive ions issuing from the electron beam and let pass only those ions having velocities very nearly perpendicular to the axis of the cylinder. These slots were of dimensions, 0.5 mm wide and 3 mm thick, requiring that the ions have 98 percent of their velocity or 96 percent of their volt-velocity perpendicular to the electron beam in order to pass through the slots. Parts *A* were cylindrical guard rings to *B*. Between *A* and *G* could be applied on the ions a retarding potential V_R. A Compton

electrometer with suitable carbon ink shunts was connected between A and B to measure currents to B.

The flow method was used to obtain a supply of hydrogen, which was admitted through a palladium tube surrounded by an electrical heating coil. The pressure used was estimated to be of the order of 2.0×10^{-4} mm Hg.

It was necessary to use electron currents of from 5 to 8 microamperes to obtain measureable positive ion currents.

For all of the data shown there was an initial velocity correction of 1.5 volts to be applied to the potential V_a. This was determined by noting the ionization potential of mercury vapor, which was not completely eliminated from the tube but was reduced to a very low pressure by liquid oxygen.

For such light ions as those of hydrogen the effect of the magnetic field upon the ions is not negligible. The effect was calculated. If ions be formed at the center of the cylinder with volt velocity V_F and pass out perpendicularly to the axis of the cylinder and are just able to reach B, in the presence of a retarding potential V_R and the magnetic field H, then

$$V_F = V_R + 300b^2eH^2/8mc^2 \text{ (volts)} \tag{4}$$

where b is the radius of the collector B in cm, e/m is the specific charge for the ion in e.s.u./gr., and H is the magnetic field in gauss. For H^+ ions, using the constants of the apparatus, this becomes

$$V_F = V_R + 0.63 \times 10^{-4}H^2 \text{ (volts)}. \tag{5}$$

For 100 and 150 gauss this correction becomes 0.63 and 1.42 volts, respectively.

Velocity Distribution of the Ions

The relative abundance of the positive ions at the various values of V_R was found by measuring the change in the electrometer current on varying V_R by a small amount ΔV, one-half of this on each side of the voltage V_R. Graphically, it was found that $\Delta V = 0.5$ volts was a small enough differentiating potential to give within the experimental error the form of the derivative curve of the total positive ion current-retarding potential curve for ions having velocities greater than 1.5 volts. The results are shown in Fig. 3. The magnetic field used was 100 gauss except in the 200 and 250 volt curves, for which it was 150 gauss. These curves were all taken at the same pressure and as shown have been reduced to equivalent electron current.

Curves of the ions without appreciable kinetic energy are not shown because the presence of mercury ions invalidated the results. It should be remarked, that, because of the magnetic field, theoretically there should be collected no H_2^+ ions having velocities of formation less than 0.3 volts. Actually a high peak is observed, coming in at about 15.5 volts electron velocity, with a velocity distribution maximum at about 1.0 volts. This is a much larger velocity than their expected temperature velocity at 25° C. It is to be remarked that the low velocity ions might be bent into small circles by the magnetic field, thereby creating an appreciable positive ion space charge which would impart to the ions some kinetic energy. Or, there

might exist an appreciable contact potential between the collecting cylinder and the defining cylinder G. Nevertheless, the corrections given by Eq. (5) were those applied.

For electron velocities up to 45 volts the maximum D of the velocity distribution curve shifts toward higher velocities as would be expected, for the electrons are acquiring sufficient velocities to produce the higher velocity ions. From 45 to 55 volts it remains approximately unchanged. Beginning

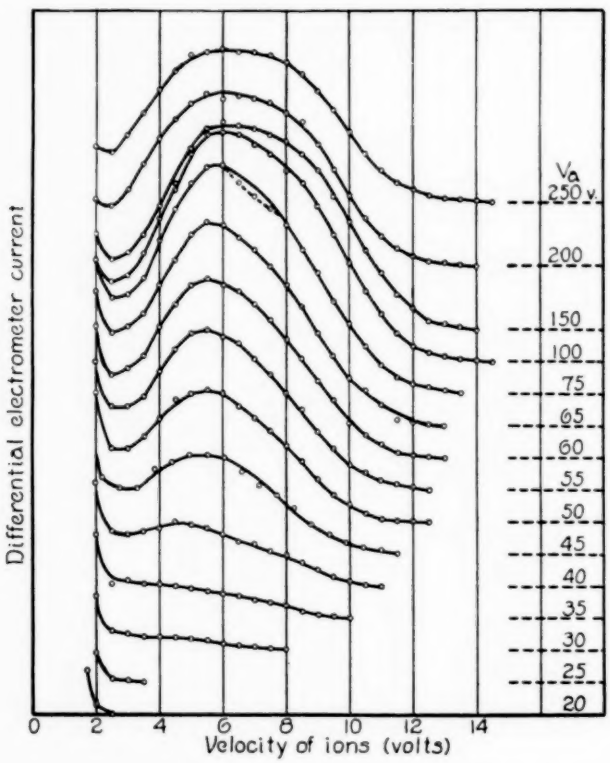

Fig. 3. Velocity distribution of the positive ions. An initial velocity correction of 1.5 volts should be applied to the values of V_a. The velocities of the ions have not been corrected for the effect of the magnetic field.

at about 60 volts the higher velocity ions increase noticeably in numbers, while the increase below the maximum is comparatively smaller. This is attributed to the yield of ions from the state e.

Ionization Potentials

Ionization potentials for those ions resulting from transitions to state d were determined by setting a certain retarding potential V_R and varying the potential V_a until positive ion current began to reach B.

Ionization potentials for those ions formed by transitions to state e required a little different procedure. Theoretically those ions having velocities between 7.5 and 11.0 volts could also be obtained by transitions to state d.

Therefore for this range the ionization potentials must be detected as upward breaks in the positive ion current vs. electron velocity curves for the various values of V_R. These results are shown in Fig. 4. In these curves the

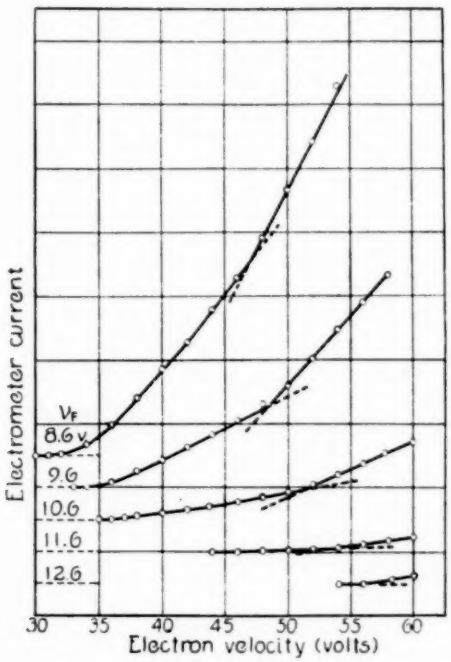

Fig. 4. Curves showing positive ion current reaching collecting cylinder against a definite retarding voltage, as a function of the electron velocity. The accelerating potential should be increased by 1.5 volts.

values of V_R have been corrected for the effect of the magnetic field. The electron velocities should however be increased by 1.5 volts, the initial velocity correction. The ionization potentials were determined and the results were plotted in Figs. 5 and 6. In Fig. 5 the straight line gives the theoretically predicted values for the state *d*, and Fig. 6 those for the state *e*.

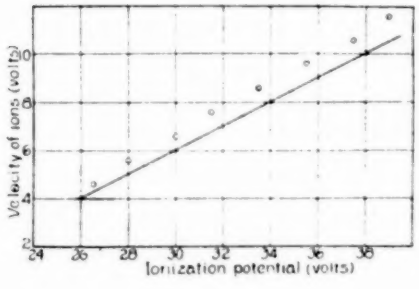

Fig. 5.

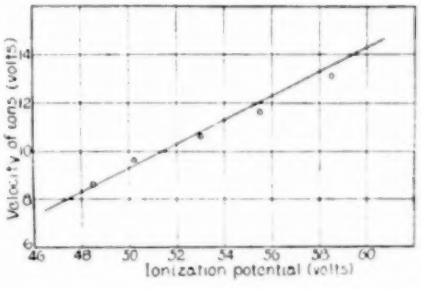

Fig. 6.

Relations between the velocities of the ions and their ionization potentials for transitions to states *d* (Fig. 5) and *e* (Fig. 6). The straight lines represent the theoretical relations and the circles represent the experimental values.

The circles give the experimental points. In these figures the above-mentioned corrections have been made.

Of the possible disturbing effects mentioned above, space charge would account for the direction of the discrepancy in Fig. 5. The effect of contact potential might cause a deviation in either direction. However, applying such a correction, the points in Fig. 6 would then lie below the straight line. But it is to be noticed that in Fig. 4 the breaks were taken at the intersections of the extrapolated straight lines, while it may be that they should have been taken at lower electron velocities, corresponding to the point where the smooth curve began to break away from the first straight line. In the last two curves of Fig. 4 the currents were quite small and the intersection with the zero axis is rather indefinite. This is to point out that the discrepancies are by no means serious.

Conclusions

The results of the present work constitute a striking confirmation of the essential correctness of the quantum mechanical theory of the hydrogen molecule. They provide a new method of attack on the general problem of molecular mechanics which will supplement the information gathered from the studies of band spectra by revealing the energy content of the unstable configurations of the molecule.

The experiments are now being extended to other gases. In conclusion, the writer wishes to express his gratitude to Professor John T. Tate and Dr. Walker Bleakney for their suggestion of the problem and for many practical aids throughout the investigation.

THE IONIZATION OF HELIUM, NEON, AND ARGON BY ELECTRON IMPACT

By Philip T. Smith

Physical Laboratory, University of Minnesota

(Received September 11, 1930)

Abstract

Quantitative measurements have been made of the total number of positive charges produced per electron per cm path at a definite pressure, in helium, neon, and argon, as a function of the energy of the impacting electrons out to 4500 volts. In helium the maximum efficiency 1.256 occurs at 110 volts, in neon 3.008 at 170 volts, and in argon 13.01 at 88 volts.

An empirical relation has been found which expresses the efficiency of ionization of helium within the experimental error for energies greater than 60 volts.

The data obtained differ considerably from that found by previous investigations, but because of the more precise length of path from which the positive ions were measured and the more accurate knowledge of the energy of the electrons as well as the elimination of secondary electrons, it is believed that the results presented here are the most accurate thus far obtained.

SEVERAL investigations have been made of the efficiency of ionization by electron impact in various gases.[1–9] Five different methods have been used, with results which are not in satisfactory agreement. The most extensive investigations were those of Hughes and Klein[3] and Compton and Van Voorhis.[1,2] After applying certain necessary corrections to the data of Hughes and Klein, Compton and Van Voorhis[2] were able to make these data qualitatively substantiate their own. Jones[4] and Bleakney[5] using a method suggested by Professor Tate measured the efficiency of ionization in Hg vapor with results which agreed only qualitatively with those of Compton and Van Voorhis.

Hummel[6] who studied Ne, A, and K by a method similar to that of Jones also agreed only qualitatively with Compton and Van Voorhis for Ne and A. The complicated effects present in the method used by Jesse[7] make it impossible to compare his results with those of the others. Finally the results of von Hippel[8] and Funk[9] cannot be reconciled at all with the results of the other observers.

Because of these discrepancies in the measured values of the efficiency of

[1] Compton and Van Voorhis, Phys. Rev. **26,** 436 (1925).
[2] Compton and Van Voorhis, Phys. Rev. **27,** 724 (1926).
[3] Hughes and Klein, Phys. Rev. **23,** 450 (1924).
[4] T. Jones, Phys. Rev. **29,** 822 (1927).
[5] W. Bleakney, Phys. Rev. **34,** 157 (1929); **35,** 139 (1930).
[6] A. D. Hummel, Thesis, University of Illinois (1928).
[7] Jesse, Phys. Rev. **26,** 208 (1925).
[8] von Hippel, Ann. d. Physik **87,** 1035 (1928).
[9] Funk, Ann. d. Physik **4,** 149 (1930).

ionization it was thought desirable to redetermine them by a method as free as possible from those sources of error which are inherent in most of the methods previously used and also to extend the work to higher voltages.

In this paper are presented the results obtained by using a method similar to that employed by Jones,[4] Bleakney[5] and Hummel.[6]

Apparatus and Procedure

The apparatus, Fig. 1, was made of copper with Pyrex insulation. It was baked out at a bright red heat before, and at about 400°C for two days after, it was placed in the tube. A Pyrex tube with no wax joints was used. It was surrounded by a solenoid to develop the magnetic field H which facilitated the separation of the positive ions from the electrons and also served to define the electron beam. The electron source was the filament F made of fine tungsten wire bent in the form of a hairpin about 1 mm wide. The holes

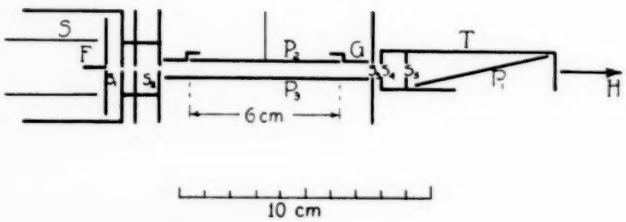

Fig. 1. Diagram of apparatus.

S_1 and S_2 were about 1.5 mm in diameter. This arrangement eliminated the presence of secondary electrons from the metal parts, since the magnetic field and not the slits defined the electron beam. Thus none of the electrons could collide with any metal until they reached the collecting plate P_1 which was connected to the grounded box T through a galvanometer G_1 (sensitivity 1500 megohms) and a set of B batteries (400 volts). S_3 was 5.5 mm in diameter while S_4 and S_5 were 5 mm in diameter.

The plate P_1 was covered with soot and, as stated above, maintained 400 volts positive with respect to T. Thus any electron which left P_1 would be in a field whose direction was nearly perpendicular to the axis of the tube and would have to go through a retarding potential of 400 volts before it could leave T. That P_1 collected all of the electrons is indicated by Fig. 2 in which the electron current to P_1, for various values of V_a, as a function of the potential of P_1 is shown.

The plate S_1, shield S, and the filament F (heated by the current from an insulated battery) were at the same potential $-V_a$ with respect to S_2 which was grounded.

The plate P_2, 6.05 cm$\times$2 cm was connected to the guard-ring G through the galvanometer G_2 (sensitivity 45,000 megohms) which measured the positive ions produced by the electrons in the 6.05 cm path directly below P_2. The positive ions were drawn out of the electron beam by an electric field between P_2 and P_3 which were 6 mm apart and maintained at 4 volts difference of potential. G and P_3 were connected together by a high resistance,

the midpoint of which was grounded, so that the speed of the electrons would not be appreciably altered after they left the last slit S_2 until they passed through S_4 which was at the same potential as S_2.

Compton and Langmuir[10] have pointed out that probability of ionization by an electron in terms of the total number of collisions made per unit path by the electron is not easy to measure nor to define accurately, and consequently it is better "to deal directly with the more accurately determined quantity, the number of new electrons produced by ionization per unit path at a specified gas pressure by an electron of given energy. This may be called

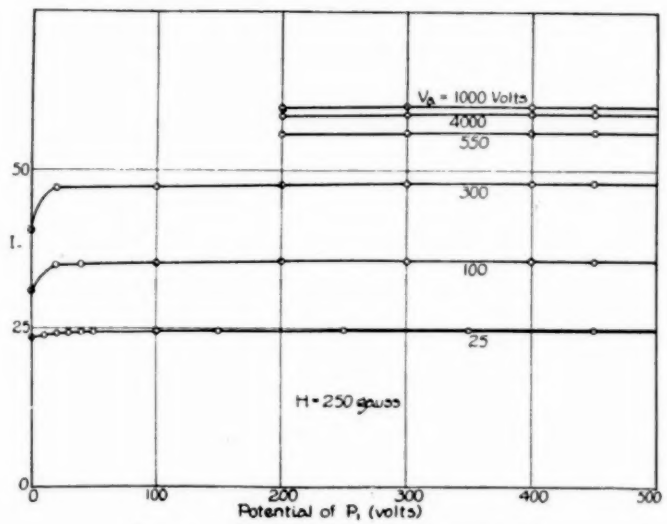

Fig. 2. Characteristics of electron trap.

the probability of ionization per unit path at unit pressure." In the present paper this quantity will be called the "efficiency of ionization," with the further specification that the temperature be 0°C.

The efficiency of ionization, ϵ, as defined above is given by the relation

$$\epsilon = (I_+/I_-)\left[(T_1T_2)^{1/2}/273lp\right]$$

where I_+ is the positive ion current collected by the plate P_2 and measured by the galvanometer G_2, I_- the electron current collected by P_1 and measured by the galvanometer G_1, T_1 and T_2 the respective absolute temperature of the McLeod gauge and apparatus, l the length of the plate P_2, and p the pressure of the gas in mm of Hg. T_1 was measured by a thermometer and T_2 by a thermocouple connected to the center of P_2 and at one edge, P_2 serving as one junction.

For He and Ne pressures from 1.0 to 1.6×10^{-3} mm of Hg were used. In argon the final results were obtained by using a pressure of 0.277×10^{-3}. At these pressures the ratio of the maximum positive ion current to plate P_2 to the electron current to P_1 was always less than 0.02, consequently the electron current could at the most not be more than 2 percent too high,

[10] Compton and Langmuir, **Rev.** of Mod. Phys. **2**, 129 (1930).

even though the new electrons from the positive ions were measured. At these pressures the chance of an electron colliding more than once before it reaches the electron trap T is small enough to be neglected.

The electron current[11] collected by P_1, which came from the ions formed within T, was smaller than the accuracy with which the total electron current could be measured.

Fig. 3 is a typical saturation curve for the positive ion current to P_2 The positive ion current to P_2 is shown as a function of the difference of potential in volts between P_2 and P_3, with the magnetic field H equal to 250 gauss, the field used throughout this investigation. Similar curves up to $V_a = 4500$

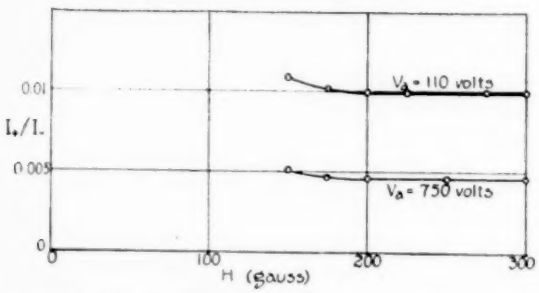

Fig. 3. Typical saturation curve for positive ions.

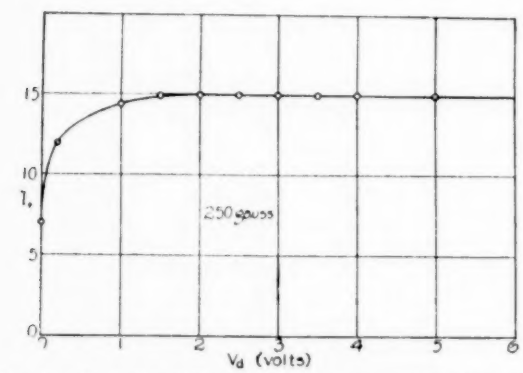

Fig. 4. The ratio of the positive ion current to the electron current as a function of the magnetic field.

volts were obtained. That none of the positive ions measured came from T was concluded, since no positive ions were collected when V_a was less than the ionization potential of the gas in the tube, with P_1 at a high potential.[12]

[11] The total current to T and P_1, was not measured by a single galvanometer, since such an arrangement would have required a well insulated set of "B" batteries which were not available. The electrical circuit was, however, arranged so that the current to either could be measured at any time without altering any of the conditions existing in the tube.

[12] The question as to whether any photo ionization might be present which would alter the values of ϵ was experimentally tested. P_2 was removed and replaced by a narrow plate to collect the ions formed by direct impact. On each side of this plate was a wider plate connected to an electrometer. The results showed that if any photo ionization did occur it was too small to effect the efficiency measurements.

Fig. 4 indicates that the ratio of the positive ion current to the electron current was independent of the magnetic field, near the value used when readings were taken. The higher ratio obtained with lower magnetic fields is explained by the spreading of the electron beam, since a negative current was collected on T with the lower fields. This current was just great enough to account for the increase in the ratio. With higher fields no electron current was collected by either S_3 or T.

The gases used were commercially pure. The helium and neon were further purified by connecting to the tube a charcoal trap immersed in liquid oxygen. The purity of the helium is indicated by the curve for helium in Fig. 7, that is, any appreciable amount of foreign gas would have resulted in ionization below the ionization potential of helium. Helium has the highest ionization potential and the lowest efficiency of any of the gases. Dr. Bleakney made an analysis with a mass spectrograph of the neon used and found a trace of helium present (not more than one percent). Helium is the only gas with an ionization potential higher than that of neon and consequently the curve in Fig. 8 would not show the presence of a small amount of helium. However the presence of one percent of He in Ne would not affect the results by more than 2/3 percent, since the efficiency is not very different for the two gases. Charcoal absorbs a little more neon than helium but the results are probably not off by more than one percent due to the presence of the helium. Bleakney found no impurities at all in the argon for which CO_2 snow in acetone was used in place of the liquid oxygen.

The pumps were sealed off from the tube by a mercury trap. (The mercury vapor was frozen out by a trap immersed in liquid oxygen.) The gas to be studied was allowed to leak into the tube through a small capillary until the desired pressure was obtained, after which the flow was cut off. No ionization could be detected before the gas was admitted, although an electron current four or five times that used in taking the readings was employed. The tube was allowed to stand for about two hours after the gas had been admitted, to be sure that a pressure equilibrium had been established between the charcoal and the gas. It was found that the variations in the pressure were less than one percent over a period of 12 hours. After a complete set of observations had been taken, readings were repeated at intervals over the entire range of accelerating potentials used. Any observation could be checked to within one percent. Curves obtained on different days checked very closely except at the highest potentials where variations of several percent occurred.

In the calibration of the McLeod gauge, etc., an attempt was made to reduce all constant errors to a minimum.

Result

Fig. 5 shows the results obtained for He, Ne, and A up to 1500 volts, (readings were taken up to 4500 volts). The efficiency of ionization as defined above is shown as a function of the accelerating potential of the electrons.

The break in the curve for argon at about 57 volts was at first hard to

account for, since the energy necessary to form A^{++} as a primary product is 43.51 volts.[13] The results of Bleakney[14] however indicate that this would be expected, due to the peculiar form of the efficiency of ionization curve for A^{++}.

Professor Tate has derved the empirical relation

$$\epsilon = 3.383(V_0/V_a)^{1/2}\left[1 - e^{-54V_0/V_a}\right]^{1/2}\left[1 - e^{-(V_a-V_0)/2.28V_0}\right]$$

which expresses the efficiency of ionization of helium within the experimental error for $V_a > 60$ volts out to 4500 volts. Below 60 volts this formula yields values of ϵ which are higher than the observed values, since the observed values approach a linear function of V_a near the ionization potential while the above formula does not.

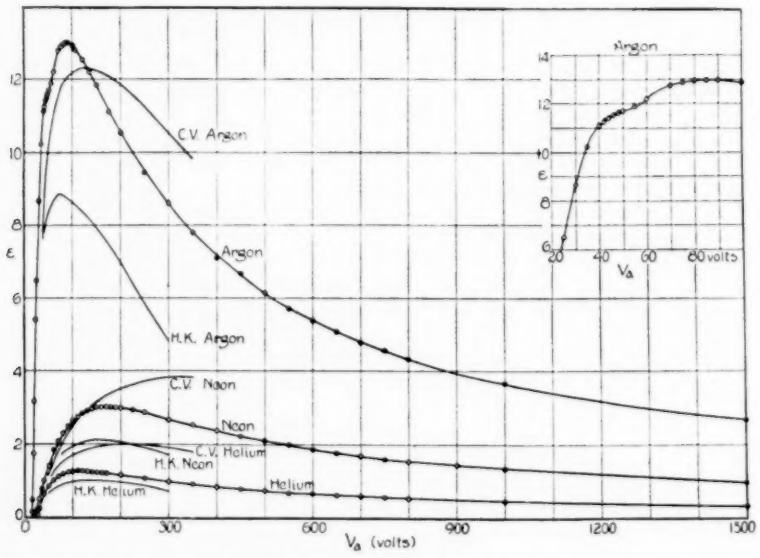

Fig. 5. The efficiency of ionization of He, Ne, and A as a function of the energy of the impacting electrons in volts, reduced to 1 mm pressure at 0°C.

It would seem that the above expression is more than a mere empirical formula, since there are in it only two constants which determine the shape of the curve, the constant 3.383 being only a scale factor.

These results were obtained with electron currents of from 1 to 3×10^{-7} amperes for $V_a < 2000$ volts, beyond which the currents used were from 8 to 10×10^{-7} amperes. For $V_a > 100$ volts the efficiency of ionization was independent of the electron current over the range 5×10^{-8} to 10^{-6} amperes, but for $V_a < 100$ volts it was found that the form of the curves began to change appreciably with electron currents greater than about 5×10^{-7} amperes. This could be accounted for by the increasing space charge at higher current densities which would decrease with increasing V_a, causing

[13] K. T. Compton, J. C. Boyce, and H. N. Russell, Phys. Rev. **32**, 179 (1928).

[14] W. Bleakney, see the following paper in this issue.

the voltage correction also to decrease with increasing V_a. In the results given here, the current density was always low enough so that this effect was not appreciable.

The temperature of the tube, about 87° C, was the same as the temperature of the solenoid and consequently the whole apparatus inside the tube came to the same temperature.

The same data are given in Fig. 6, but in order to show the results out

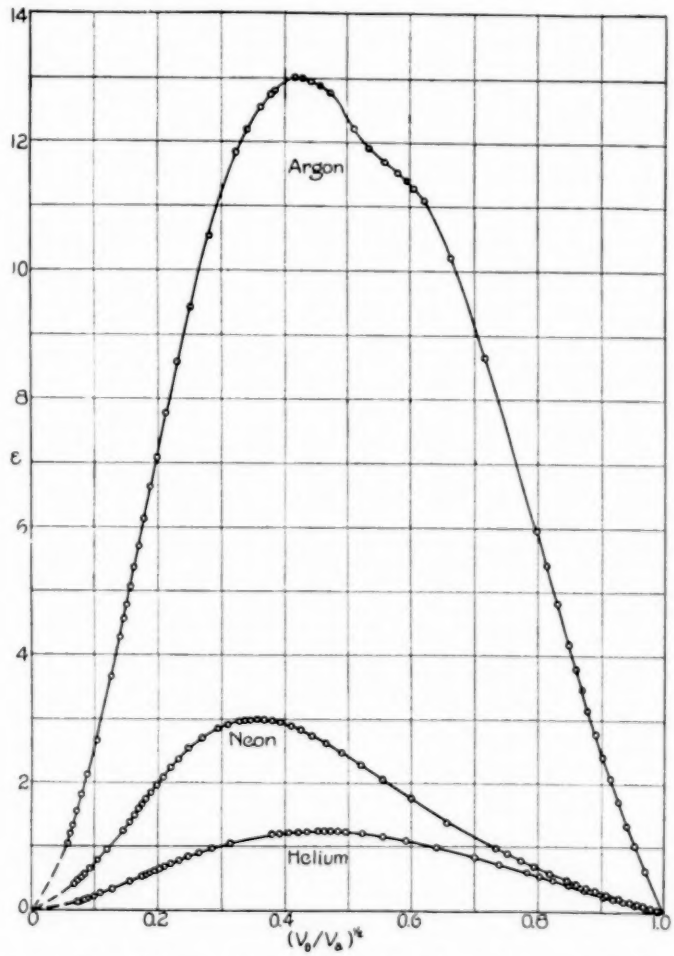

Fig. 6. The efficiency of ionization of He, Ne, and A as a function of $(V_0/V_a)^{1/2}$, reduced to 1 mm pressure at 0°C.

to 4500 volts the efficiency is shown as a function of $(V_0/V_a)^{1/2}$ when V_0 is the ionization potential of the gas and V_a the accelerating potential of the electrons.

The results are also given in the following table. The efficiency of ionization as defined, represents the average total number of positive charges per electron per cm path at 1 mm pressure and 0° C. The values of V_a have been corrected for contact e.m.f.'s initial velocity, etc., in the following manner.

To obtain a correct voltage scale the curves in Fig. 7 were drawn.[15] The extrapolated straight lines were assumed to be the correct curves, the curved part being due to the velocity distribution of the electrons. All of the

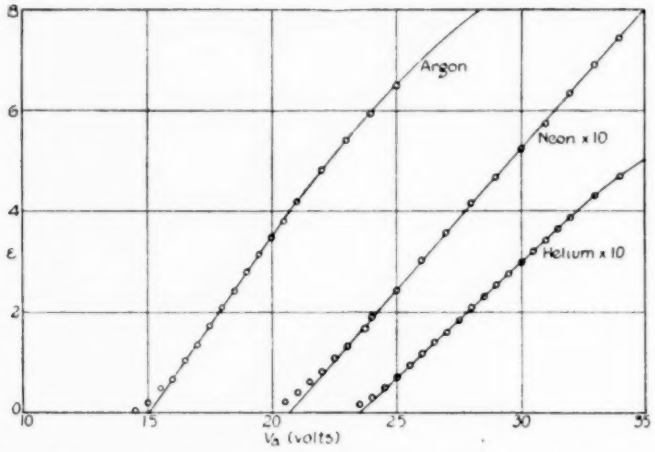

Fig. 7. The efficiency of ionization as a function of the energy of the impacting electrons, near the ionizing potential. The ionization potential of helium was assumed to be 24.48 volts, that of neon 21.47 volts, and that of argon 15.69 volts.[15]

curves do not show the same correction since the apparatus was changed several times and new filaments inserted.

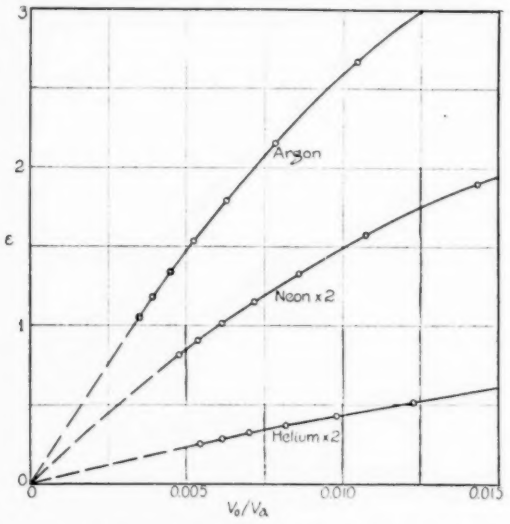

Fig. 8. The efficiency of ionization as a function of (V_o/V_a) for large values of V_a.

The curves in Fig. 7 also indicate that the efficiency of ionization is a linear function of the energy of the impacting electrons near the ionization potentials of the gases studied, whereas at higher velocities, Fig. 8, the

[15] The values of ionization potentials were obtained from the Int. Crit. Tables, Vol. VI, p. 70.

efficiency apparently becomes inversely proportional to the energy. This was found to be approximately true with beta-particles in an article by W. Wilson.[16] J. J. Thomson[17] theoretically arrived at a formula which represents the efficiency of ionization as being inversely proportional to the energy of an impacting electron with energy much greater than the minimum ionizing energy. The formula does not, however, at all represent the observed data at lower energies and yields values much too low at higher energies. Bohr[18] was able however partly to account for this discrepancy by considering the ionization due to the secondary electrons emitted in the process of forming the ions. In the present investigation this factor

TABLE I. *Efficiencies of ionization expressed as numbers of positive charges per electron per cm path per mm pressure at 0°C for various electron velocities.*

V_0	He	Ne	A	V_0	He	Ne	A
16.0			0.22	70	1.110	2.110	12.75
16.5			0.58	75			12.87
17.0			0.93	80	1.178	2.340	12.95
17.5			1.29	85			12.98
18.0			1.65	90	1.220	2.520	13.00
18.5			2.00	100	1.245	2.660	12.90
19.0			2.35	105	1.251		12.80
19.5			2.70	110	1.256	2.770	12.75
20.0			3.07	115	1.255		
20.5			3.40	120	1.250	2.860	12.53
21.0			3.75	130	1.247	2.930	
22.0		0.032	4.65	135			12.20
22.5		0.057		140	1.241	2.964	
23.0		0.087	5.12	150	1.228	2.987	11.83
23.5		0.118		160	1.216	3.000	
24.0		0.142	5.62	170	1.200	3.008	
25.0	0.022	0.198	6.16	175			11.10
25.5	0.045			180		3.005	
26.0	0.069	0.253		190		2.998	
26.5	0.092			200	1.149	2.988	10.53
27.0	0.114	0.307		225		2.935	
27.5	0.138			250	1.060	2.867	9.43
28.0	0.161	0.365		300	0.971	2.710	8.58
28.5	0.184			350	0.902	2.541	7.78
29.0	0.207	0.420		400	0.836	2.367	7.08
29.5	0.229			450	0.778	2.199	6.64
30.0	0.251	0.476	8.43	500	0.728	2.081	6.13
32.0	0.340	0.588		550	0.685	1.950	5.73
34.0	0.431	0.699		600	0.643	1.840	5.37
35.0			10.08	650	0.612	1.740	5.07
36.0	0.515	0.803		700	0.584	1.664	4.78
38.0	0.583	0.903		750	0.558	1.580	4.55
40.0	0.633	1.000	10.93	800	0.530	1.517	4.32
42.0			11.18	900		1.390	
44.0			11.39	1000	0.448	1.290	3.66
45.0	0.760			1500	0.328	0.950	2.67
46.0			11.52	2000	0.260	0.788	2.15
48.0			11.61	2500	0.215	0.663	1.79
50.0	0.860	1.470	11.68	3000	0.183	0.575	1.53
55.0	0.940		11.87	3500	0.162	0.510	1.34
60.0	1.025	1.830	12.15	4000	0.142	0.455	1.18
				4500	0.127	0.407	1.05

[16] W. Wilson, Proc. Roy. Soc. **85**, 240 (1911).
[17] J. J. Thomson, Phil. Mag. **23**, 449 (1912).
[18] N. Bohr, Phil. Mag. **30**, 581 (1915).

$q = 2.78 \times 10^{-17} \epsilon$

however would be negligible, since the number of secondary electrons would be of the same order of magnitude as the positive ion current. A beam of electrons of this magnitude could not produce an appreciable number of ions, no matter what their energy might be.

The writer hopes in the near future to study the efficiency at higher energies since the present apparatus was not suitable for potentials greater than 4500 volts.

Discussion

A comparison of the results of the present investigation for Ne, He, and A is shown in Fig. 5. The results of the other observers have been reduced to the same temperature and pressure conditions. The corrections which Compton and Van Voorhis[2] applied to Hughes' and Klein's data have not been made, although the temperature of their tube was assumed to be 60° C.[2]

Because of the definite length of path from which the positive ions were measured, and the more accurate knowledge of the energy of the impacting electrons as well as the elimination of secondary electrons, it is believed that the results presented here are more accurate than those of the previous investigations.

Although Hummel used the same method, the distorted fields in the ionizing chamber and the presence of secondary electrons from the slits which defined his electron beam, makes a comparison with his data difficult.

It is a pleasure for the writer to express here his gratitude to Professor John T. Tate, who suggested the method used and under whose guidance this work was carried out. Thanks are also due to Dr. Walker Bleakney for his constant interest and many suggestions.

IONIZATION POTENTIALS AND PROBABILITIES FOR THE FORMATION OF MULTIPLY CHARGED IONS IN HELIUM, NEON AND ARGON.

By Walker Bleakney

Physical Laboratory, University of Minnesota

(Received September 11, 1930)

Abstract

The multiply charged ions in helium, neon and argon have been studied with a mass spectrograph previously described. In helium the He^+ ion showed up strongly but only faint evidence for the formation of He^{++} was found and no quantitative data for its relative intensity could be obtained. Neon yie ded the three ions Ne^+, Ne^{2+} and Ne^{3+} as the result of single electron impacts occurring respectively at minimum electron energies of 21.5, 63, and 125 volts. Curves which illustrate the efficiency for the formation of these ions expressed in number of ions per electron per cm per mm pressure at 0°C as a function of the electron velocity exhibit maxima for Ne^+ and Ne^{2+} of 2.75 and 0.16 at 150 and 250 volts respectively. In argon the five ions A^+, A^{2+}, A^{3+}, A^{4+} and A^{5+} were observed. The ionization potentials for the first four were found to be respectively, 15.7, 44, 88 and 258 volts for single impact. The efficiency curves show maxima of 11.4, 1.1 and 0.04 at 50, 115 and 250 volts for A^+, A^{2+} and A^{3+} respectively. In the curves for Ne^{2+} and A^{4+} are found several upward breaks beyond their ionization potentials which indicate other higher critical potentials for their formation.

Introduction

A METHOD of studying the multiply charged ions produced by electron impact in gases at low pressures has recently been described[1] and some results in mercury vapor and hydrogen have been reported. It is the purpose of the present paper to describe the results of a similar study of the ionization products in the rare gases—helium, neon and argon. Barton[2] has previously studied argon with a mass spectrograph. Certain improvements in the present method over those formerly employed have yielded new data, particularly in the experiments on neon and argon.

Apparatus and Procedure

The apparatus employed in this investigation was essentially the same as that used in the study of ions in mercury vapor and hydrogen.[1] The reader is therefore referred to this earlier work for a detailed description of the method. The gases were admitted to the apparatus through a fine capillary at one end of the tube and the pressure could be varied by opening or closing with a mercury cut-off constrictions of different sizes in the pumping line leading from the other end of the tube. The pressures found suitable varied from 5 to 50×10^{-5} mm Hg. Helium from a steel drum was purified by passing it over charcoal immersed in liquid oxygen. The neon and argon were admit-

[1] W. Bleakney, Phys. Rev. **34**, 157 (1929); **35**, 139 (1930); **35**, 1180 (1930).

[2] H. A. Barton, Phys. Rev. **25**, 469 (1925).

ted to the apparatus directly from the Pyrex containers supplied by the Air Reduction Company without further purification. A preliminary study of the ions showed the helium and argon to be quite pure while the neon contained a slight amount (less than one percent) of helium. There was always present in the tube, however, even before any gas was admitted through the capillary, traces of some impurities which were identified as hydrogen, water vapor, and carbon monoxide. The number of ions due to these impurities was very small compared to those of the gas under investigation necessitating a correction usually of about one percent in the cases of argon and neon. It was only in the determination of ionization potentials, where it was necessary to measure very small currents, that the impurities caused any trouble, and here their effect was minimized by proper adjustment of pressure and current density. In all the results presented in this paper the data have been corrected as far as possible for the effect of impurities.

Results

Helium. The singly charged He^+ ion formed, of course, a very strong peak in the analyzer. Unfortunately for this work the H_2^+ ion has the same e/m as He^{2+} and since there was always, as mentioned above, a trace of hydrogen present in the tube it was impossible to get any quantitative measure of the number of He^{2+} ions produced. However, the evidence at electron velocities of several hundred volts pointed toward the existence of He^{2+} but certainly less than one percent of all the helium ions formed were doubly charged.

Neon. The three ions Ne^+, Ne^{2+}, and Ne^{3+} were found in neon and their ionization potentials were determined from the data shown in Fig. 1. Here the maximum heights of the peaks in the e/m analysis curves are plotted as functions of the electron velocity expressed in volts. With carbon dioxide snow on the trap a sufficient amount of mercury vapor remained in the tube to calibrate the voltage scale by means of the Hg^+ ion whose ionization potential was assumed to be 10.4 volts. Thus all of the ionization potentials could be measured without altering any of the conditions in the tube. The critical potentials obtained for ionization at single impact together with the estimated limits of experimental error are given in the second column of Table I. The agreement with the values calculated from spectroscopic data demonstrates the reliability of the method The experimental error increases with increasing charge on the ion because of decreasing intensity and lack of complete resolution

Table I. *Ionization potentials in neon for single electron impact.*

Ion	Experimental	Spectroscopic
Hg^+	10.4 volts	10.39[3] volts
Ne^+	21.5 ± 0.1	21.47[3]
Ne^{2+}	63.0 ± 0.5	62.4[4]
Ne^{3+}	125.0 ± 1.0	

[3] International Critical Tables VI, p. 71.

[4] H. N. Russell, K. T. Compton and J. C. Boyce, Proc. Nat. Acad. Sci. **14**, 280 (1928).

The curves for Ne^{2+} and Ne^{3+} shown in Fig. 1 have a peculiar shape, unlike the others, suggesting more than one process for the formation of these ions. Particularly in the case of Ne^{3+} the curve shows two definite upward breaks, the first occurring in the neighborhood of 143 and the second at about 157 volts. These are perhaps to be correlated with the energies necessary to remove different electrons from the neon atom. For instance it may require 125 volts to remove three $2p$ electrons, 143 volts to remove two $2p$ and one $2s$ at a single blow and 157 volts to remove one $2p$ and two $2s$ electrons in one group, all three processes resulting in Ne^{3+} ions.

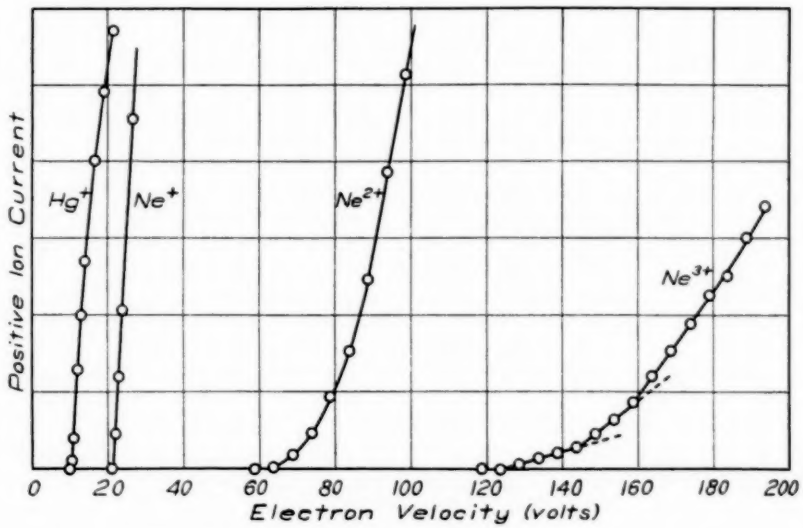

Fig. 1 Curves showing the ionization potentials in neon. The ordinate scale is an arbitrary one and differs for each curve.

The areas under the peaks in a set of runs carried out at various electron velocities were measured to determine the fractions of the total current carried by he several types of ions. The results are shown in Fig. 2 where the ordinates represent the percent of the total positive ion current to be assigned to the Ne^{+}, Ne^{2+} and Ne^{3+} ions. It will be noticed from the figure that beyond 200 volts approximately 88 percent of the current is made up of singly charged ions while doubly charged ions account for about 11 percent.

The data of Fig. 2 combined with the measurements of the total ionization given by Smith[5] enable one to calculate the probability of ionization for each type of ion. The result is obtained by multiplying the ordinate of Fig. 2 by the total ionization for that particular value of the electron velocity as given by Smith and dividing by the number of charges on the ion. Figure 3 shows the results of this calculation where the ordinates represent the probabilities of ionization expressed in numbers of ions per incident elecron per cm path per mm pressure at 0°C as a function of the electron velocity. The curves for Ne^{+} and Ne^{2+} exhibit broad maxima of 2.75 and 0.16 at 150

[5] P. T. Smith, see the preceding paper of this issue.

and 250 volts respectively while that for Ne^{3+} shows no maximum in the range studied.

Argon. A study of the mass spectrum of argon revealed the five ions A^+, A^{2+}, A^{3+}, A^{4+} and A^{5+} each one formed, it is believed as the result of a

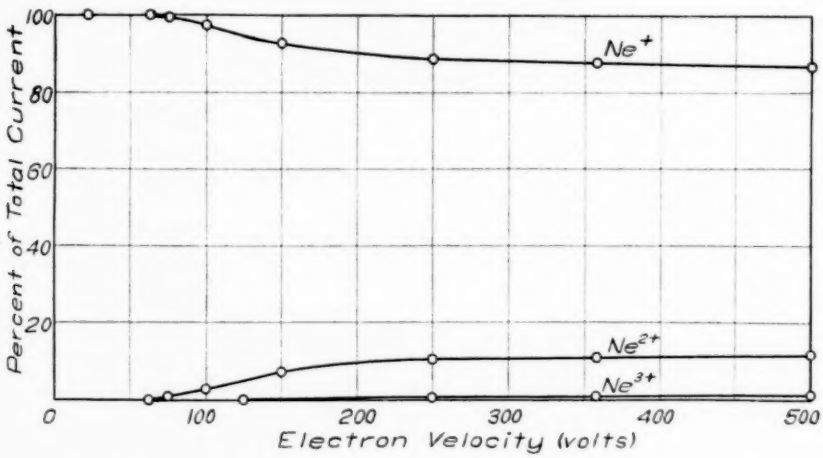

Fig. 2. Percent of total positive ion current ascribed to the different ions.

single electron impact. The intensity of A^{5+} was so small that no attempt was made to measure the number quantitatively. It can only be said that its formation certainly occurs at electron velocities below 500 volts. The ioniza-

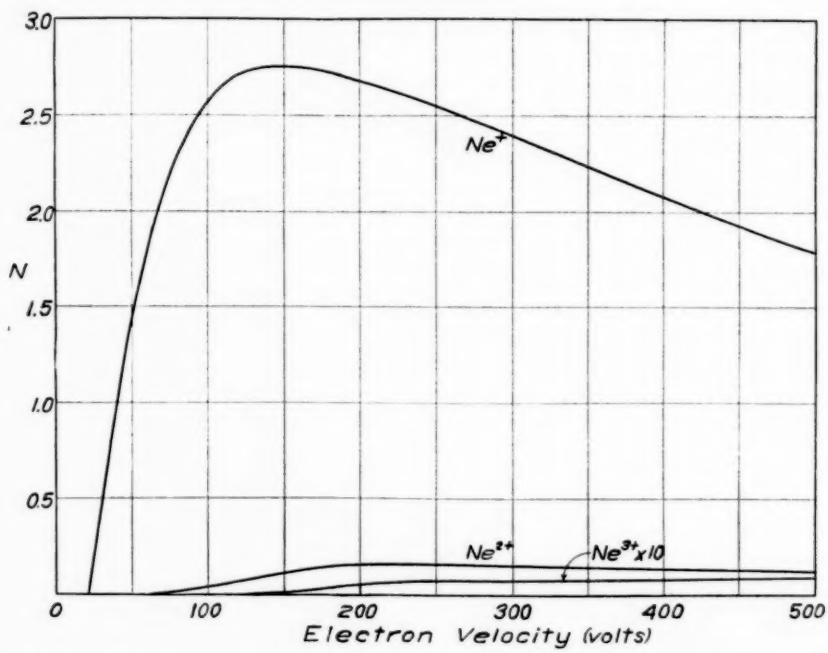

Fig. 3. Actual number of ions, N, formed per electron per cm per mm pressure at 0°C.

tion potentials for the first four ions were determined from the data shown in Fig. 4 and the values are given in Table II. It will be seen that the agreement with the spectroscopic values are quite satisfactory. The value 44.0 for A^{2+}

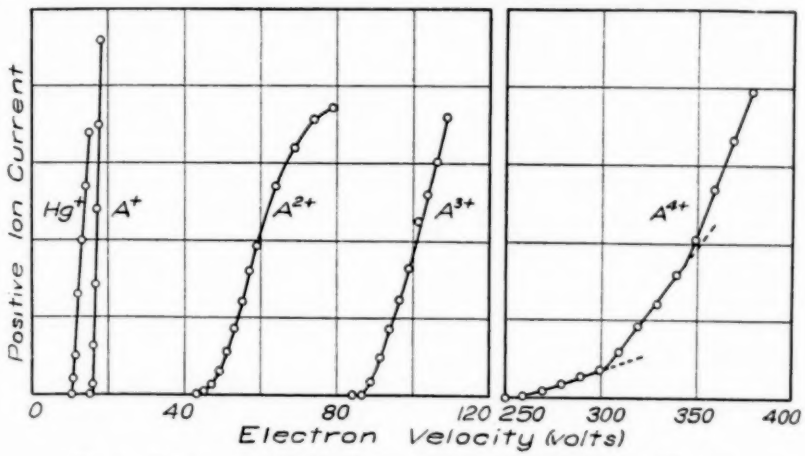

Fig. 4. Curves showing the ionization potentials in argon. The ordinate scale is an arbitrary one and differs for each curve.

checks quite well that found by Barton[2] which becomes 45.8 when his voltage scale is corrected to make A^+ appear at 15.7 volts.

TABLE II. *Ionization potentials in argon for single electron impact.*

Ion	Experimental	Spectroscopic
Hg^+	10.4 volts	10.39[3]
A^+	15.7 ±0.1	15.69[3]
A^{2+}	44.0 ±0.5	43.51[6]
A^{3+}	88 ±1	
A^{4+}	258 ±3	
A^{5+}	Less than 500	

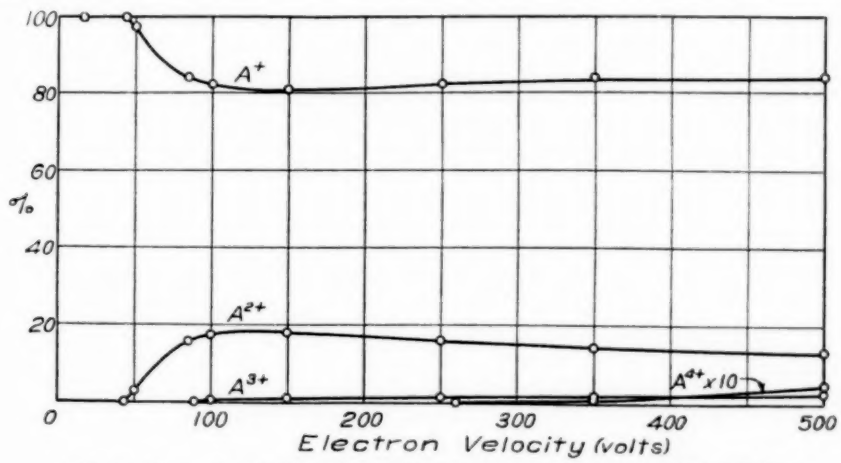

Fig. 5. Percent of total positive ion current ascribed to the different ions.

[6] K. T. Compton, J. C. Boyce and H. N. Russell, Phys. Rev. **32**, 179 (1928).

Like neon, the curves for the multiply charged ions in argon show peculiar shapes indicating more than one process of formation, and especially is this true of the fourth ion where upward breaks occur in the neighborhood of 300 and 340 volts. In all of the runs made these breaks consistently appeared but the values of the abscissas where they began did not check very well because of the difficulty encountered in holding the magnetic field perfectly constant. Hence the values given may be in error by several volts. It is hoped that these phenomena may be more carefully investigated in future work.

The fractions of the total positive ion current carried by the several ions are illustrated in Fig. 5. It appears that at least 80 percent of the current may always be ascribed, under the conditions of this experiment, to the singly charged ion in the range studied. Using again the data of Smith[5] the probabilities of producing the first four ions as a function of the electron velocity have

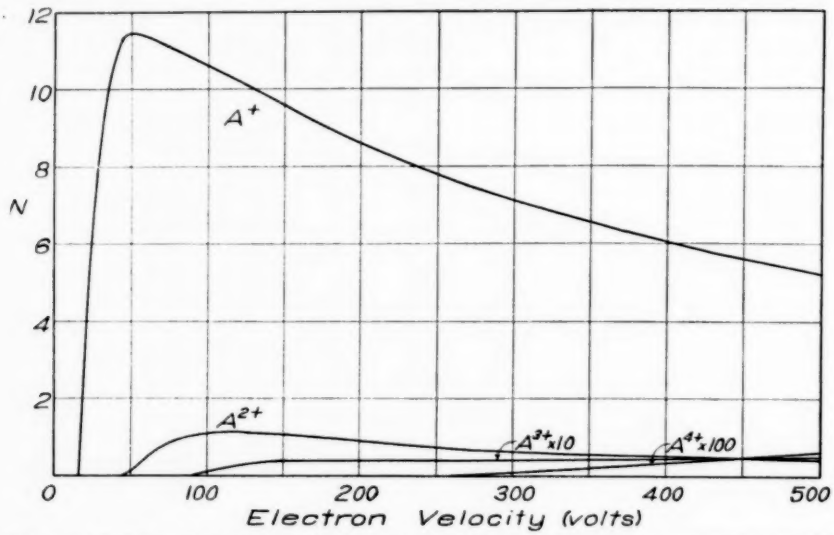

Fig. 6. Actual number of ions, N, formed per electron per cm per mm pressure at 0°C.

been calculated and are given by the curves of Fig. 6. The A^+ ion rises very sharply to a maximum value of 11.4 at 50 volts while the A^{2+} ion reaches a value of 1.1 at 115 volts. The number of A^{3+} ions shown only a very broad maximum of 0.04 beyond 150 volts and the A^{4+} curve continues to rise as far as 500 volts. The position for the maximum in the A^+ curve coincides very well with that observed by Barton[2] but none of the upward breaks observed by him beyond this point were found, probably because the present work was carried out at much lower pressures.

It is believed that work of this nature is of sufficient interest and importance to merit further investigation along the same line. It is planned, therefore, to extend the experiments during the next year to other gases and vapors in an attempt to gain further information on the mechanism of ionization by electron impact.

The author is ever grateful to Professor John T. Tate for his keen interest and helpful guidance during the course of this work.

THERMIONIC EMISSION OF OXIDE COATED CATHODES CONTAINING A Ni-Ba ALLOY CORE

By N. C. Beese
Westinghouse Lamp Co., Bloomfield, N. J.

(Received September 8, 1930)

Abstract

An appreciable increase in thermionic emission from oxide coated filaments has been obtained by introducing a small percentage of metallic barium (approximately 0.15 percent) into the nickel core material. Comparisons made on the electron emission of this alloy with pure nickel and also with the nickel alloy after the barium had been extracted always showed the influence of barium in the base metal.

Introduction

SEVERAL theories have been advanced to account for the activity of an oxide-coated cathode. One explanation requires metallic barium* on the surface of the oxide coating.[1,2,3,4] More recent investigations[5,6] indicate the influence of the core material. The following explanation of enhanced emission from oxide-coated cathodes has been given by Reimann and Murgoci.[5] The thermionic activation is accompanied by coating the surface of the core metal by a monatomic layer of barium or a double atomic layer of barium and oxygen. In either case the core metal acquires a high electron emissivity, and the electrons pass from the metallic core to the oxide coating thermionically. The electrons are then carried to the exterior surface of the coating by circulating barium atoms. The thermionic emission of the cathode as a whole is limited either by the coating or by the core,—whichever of the two systems has the lesser thermionic emissivity.

Lowry[6] has indicated the importance of the core metal in oxide-coated filaments. He finds that Konel metal filaments give usable thermionic currents at much lower temperatures than similarly coated platinum filaments. The large thermionic currents at comparatively low temperatures in the case of coated Konel filaments suggested the assumption that thermionic currents originated at the layer of barium atoms occluded on the core. The electrons emitted from this surface diffuse through the interstices in the oxide coating into the vacuous space.

Since metallic barium seems to be the active agent in releasing an abundance of electrons from an oxide-coated cathode, a small continuous supply of

* Barium is used to represent all of the alkaline earth metals.

[1] Koller, Phys. Rev. **25**, 671 (1925).

[2] Espe, Wiss. Veroff. aus dem Siemens Konzern **5**, 29 and 46 (1927).

[3] Rothe, Zeits. f. Physik **36**, 737 (1926).

[4] Becker, Phys. Rev. **34**, 1323 (1929).

[5] Reimann and Murgoci, Phil. Mag. [VII] **9**, 440 (1930).

[6] Lowry, Phys. Rev. **35**, 1367 (1930).

barium atoms from the core material added to that from the decomposed BaO coating should produce and maintain a somewhat larger source of electrons than if the coating alone furnished the source. If an enhanced emission is due to the core surface being partially covered with adsorbed barium atoms, an internal source of metallic barium should be very desirable in furnishing a uniform layer of adsorbed atoms. This resembles the process of emission from thoriated tungsten filaments. If the large emission from oxide-coated filaments is due to barium atoms adsorbed on the exterior oxide surface, the barium from the core would augment the supply furnished by the BaO. Besides increasing the activity of the filament, the migration of the metallic barium atoms from the volume of the core should maintain an increased emission for a considerable period of time. Whether the barium atoms remain at the core-coating interface or are carried to the surface of the oxide cannot be determined by the experiments to be described. However their contribution to the total emissivity of the filament is quite noticeable.

Method and Result

An alloy containing approximately 0.15 percent metallic barium in an essentially nickel base was obtained from the A. C. Spark Plug Company of Flint, Michigan. This alloy was formed into a ribbon 0.025 inch $\times$ 0.002 inch. In the comparison with pure nickel filaments, a piece of pure nickel wire was drawn and rolled to the same dimensions. The filaments were coated by spraying them with a mixture of equal weights of $BaCO_3$ and $SrCO_3$ in an amyl acetate suspension, or they were coated by passing them through a water-suspension of the carbonates followed by baking in an atmosphere of CO_2. The filaments were mounted in structures similar to the UX-281 Radiotrons.

The tubes were exhausted with a two-stage mercury condensation pump backed by a Cenco oil pump. A liquid-air trap was placed between tubes and pumps. Pressures of about 10^{-5} mm of mercury as measured on a McLeod gauge were obtained before the "getter" was flashed and the tubes sealed off

Four sets of tubes of three each were made as follows:—(1) and (2) Alloy filaments and pure nickel filaments respectively having a heavy coating weight of carbonate mixture; (3) and (4) alloy filaments and pure nickel filaments respectively having a light coating weight of carbonate mixture. The heavy coating of carbonates was applied by the "spray" method and had 8.0 mg of carbonate mixture per cm^2 of surface. The light coatings were applied by the "drag" method and had 2.3 mg of carbonates per cm^2 of surface.

Fig. 1 indicates the relative emission currents obtained by averaging the values from the first two types of filaments. The thermionic emissions in milliamperes per square centimeter of filament surface are plotted as ordinates and times are plotted as abscissae. Both types of filaments were operated with an energy input of 4 watts per cm^2 of radiating surface. This value was chosen as it is the operating condition of filaments in most commercial tubes. During life the tubes had 220 volts A.C. applied between filaments

and plates while for test purposes the measurements were made with 150 volts D.C. applied to the plates. The thermionic emissions from the pure nickel filaments were nearly constant throughout the 500 hours life test. The alloy filaments had initial emissions about equal to the emission from

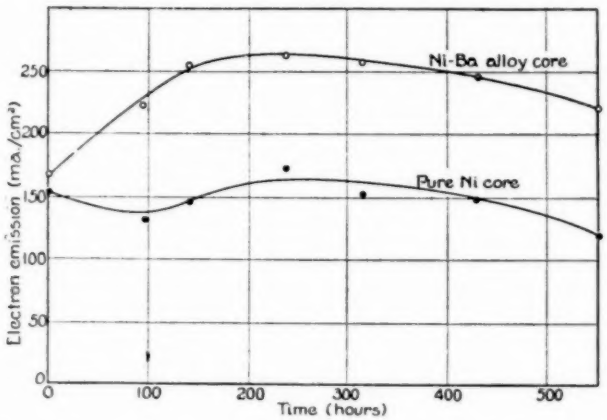

Fig. 1. Comparison of electron emission from pure Ni and alloy cores coated with a heavy coating weight of oxides.

the pure nickel filaments. This initial emission in both cases is attributed to the oxide coating and the activity of the pure nickel filament throughout its life is due to the oxide or the products of decomposition of the oxide. During operation the alloy filaments gave a constantly increasing emission for the first 150 hours, attaining a value about 70 percent larger than that of the pure nickel filaments. The larger emission was then maintained throughout the remainder of the life test. This increased emission is attributed to the fact that barium was slowly diffusing out of the volume of the core material and becoming adsorbed metallic barium at the core-coating interface or on the oxide surface. The emission from the pure nickel filaments was satisfactory for radio-tube purposes, and is the activity generally found in UX-281 type tubes.

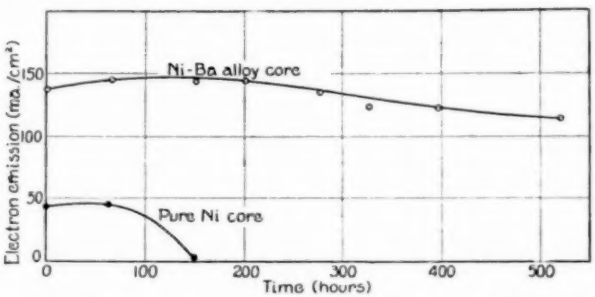

Fig. 2. Comparison of electron emission from pure Ni and alloy cores coated with a light coating weight of oxides.

In Fig. 2 is depicted the relative values of emission from filaments coated with a light coating weight of oxides. The activity of the pure nickel

filaments was low initially and had a life of only 150 hours, while the activity of the alloy filaments was comparable to that of the pure nickel filaments coated with the heavy coating weight of oxides. In this comparison the barium from the core accounts for nearly all the useful thermionic emission. It has been the writer's experience that a low initial emission and a relatively short useful life is generally associated with very light coating weights of carbonates.

Having thus accounted for the appreciable differences in thermionic activity of the two kinds of coated filaments, operated for at least 500 hours with a filament energy consumption of about 4 watts per cm^2, a further test was applied. A piece of the barium-nickel alloy filament was heated in a well exhausted vacuum tube to approximately 1300°C until the barium had been diffused to the surface of the filament and evaporated. Initially the current drawn from the filament was of the order of 25 m.a. while after this

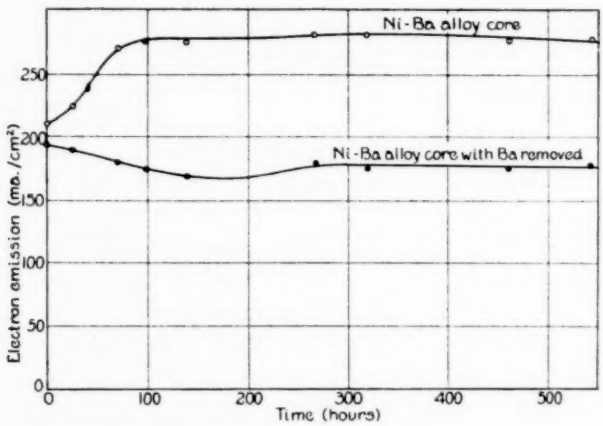

Fig. 3. Comparison of the activity of an alloy core filament with one having its barium content removed.

vacuum treatment currents of only a few microamperes could be obtained. This filament, supposedly free from barium content, was coated with a coating weight of 3.5 mg of carbonates per cm^2, together with an alloy filament that had not received the preliminary vacuum treatment. Measurements taken at intervals during the life test of these two tubes revealed that the treated filament corresponded to the pure nickel type having a constant activity, while the untreated wire gave the characteristic alloy filament type of life history. These data are recorded graphically in Fig. 3 and show the great similarity to the curves of Fig. 1.

The data recorded in the three graphs were taken under the conditions that 4 watts of energy were being radiated per cm^2 of filament area, and do not show the actual differences in activity because of space charge limitation with 150 volts plate potential. A lower filament temperature, such as that produced by a radiation of 2 watts per cm^2, would give a better indication of the relative differences in emissivity and would produce much larger ratios,

but the chosen value of 4 watts per cm² is representative of the normal operation of most commercial tubes.

Fig. 4 shows the relation between filament temperatures in watts per cm² and electron emission in m.a. per cm². Curves *A* and *B* are taken from part of the data of Fig. 1 at the time $t=240$ hours, while curves *C* and *D* are taken

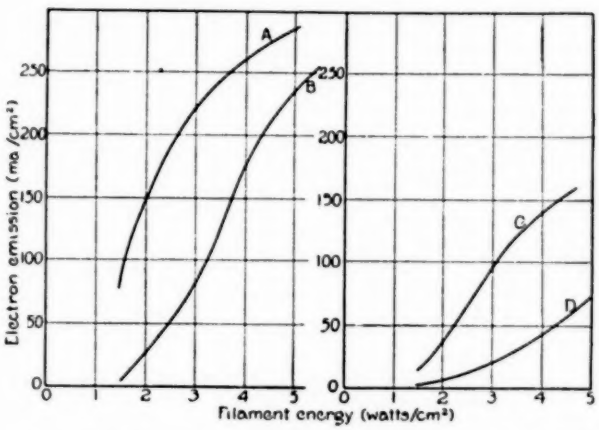

Fig. 4. Curves *A* and *B* are associated with data in Fig. 1 at $T=240$ hours; Curves *C* and *D* are initial values associated with data of Fig. 2 at $T=0$ hours.

from part of the data of Fig. 2 at the time $t=0$ hours. The curves represent the averages of the various groups of tubes of 3 each. The slopes of the curves, especially at the higher plate currents, indicate the effect of space charge.

Conclusion

The operating life history of the filaments recorded in the three graphs shows the increased activity obtained from oxide-coated cathodes that have a slight amount of metallic barium contained in the nickel core. This is especially true in the filaments covered with a light coating weight of oxide. The core material, in this case at least, has an important influence on the amount of emission.

SHOT EFFECT OF THE EMISSION FROM OXIDE CATHODES

By H. N. Kozanowski and N. H. Williams
University of Michigan

(Received August 23, 1930)

Abstract

Experimental procedure in the study of fluctuations in the space current of a thermionic emitter is outlined. A new method of measuring *shot-circuit impedance* is introduced. Conditions under which the observed fluctuations may be applied to determine the electronic charge are pointed out. A method is described whereby the frequency of oscillating circuits used in this investigation may be determined and controlled. An investigation has been made of the fluctuations associated with the emission from barium-strontium oxide cathodes, particularly in the space charge region. The presence of positive ions in the emission from oxide coatings has been experimentally verified. These positive ions moving in an electron space charge cause abnormally high shot-fluctuations in an aperiodic circuit at high amplifier frequencies. The characteristic fluctuations associated with the emission from oxide cathodes have been reproduced in a vacuum tube of special design in which positive ions from an independent Kunsman potassium ion emitter interact with electron space charge about a metal emitter. This is taken as evidence that the same process goes on in the emission from barium-strontium oxide cathodes. Some results obtained in a study of the shot effect of films evaporating from a tungsten wire are included.

THE shot effect has been successfully used in the determination of electronic and ionic charge by an entirely independent method. The emitters used for electronic currents in these determinations have been pure metals such as tungsten or thoriated tungsten. Williams and Huxford,[1] in the determination of the positive ion charge, used a Kunsman potassium ion emitter. This work was done at shot-amplifier frequencies in the region of 100,000 cycles per second. It was found that even at these frequencies, abnormal fluctuation voltages occur in the case of certain oxide electron emitters. It was to discover the underlying mechanism of these fluctuations that this investigation was carried out. A brief description of the apparatus and experimental procedure follows.

The Shot Circuit and Amplifier

An experimental arrangement for studying the shot effect of thermionic currents is shown in Fig. 1. The vacuum tube *S*, consisting of a collector plate and an emitter is mounted in a shielding compartment. The emitter is heated by a storage battery located outside this compartment. The accelerating potential is applied to the collector plate through a wire-wound resistor *R*. It can be seen from the diagram of Fig. 1 that the positive end of the high potential battery is grounded to the shield. The negative terminal

[1] N. H. Williams and W. S. Huxford, Phys. Rev. **33**, 773 (1929).

is connected to the filament leads, which are carefully insulated from direct current grounds, but are kept at ground potential for high frequency currents by the use of a one microfarad condenser having very low leakage current.

If the emitter is heated by means of the storage battery, and a positive potential is applied to the collector plate through the resistor R, electrons will flow from the emitter to the collector. The value of the electron space current is given by the direct current milliameter A. If the electron stream were perfectly continuous, only a direct difference of potential would exist between A and B equal to $I_0 R$. But since the arrival of electrons at the plate is a discontinuous process, voltage fluctuations will occur across the resistance AB. These fluctuations will be called the "shot voltage" between A and B. The space current and the space charge conditions in the tube can be controlled by variation of the emitter heating current and the accelerating potential across the tube.

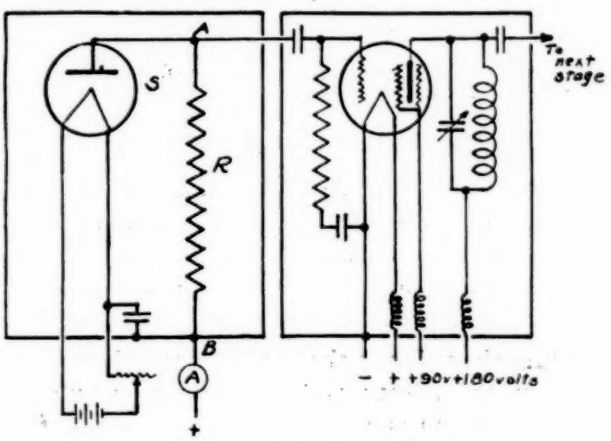

Fig. 1. Aperiodic shot effect.

The shot voltage developed across AB is impressed on the grid-filament circuit of a tuned-plate five-stage amplifier employing screen-grid tubes. Thus a narrow band of frequencies from the total "shot voltage" is selected and amplified. Coupled loosely to the tuned-plate circuit of the last amplifier tube is a coil of a few turns of wire. Voltages induced in this coil by alternating currents in the plate circuit cause current to flow through a 990 ohm vacuum thermal junction connected aross it. The magnitude of the thermoelectromotive force is directly proportional to the heating of the junction and hence to the square of the current in the circuit or to the square of the voltage across it. In this manner a direct current galvanometer across the thermoelement is used to detect high frequency voltages.

It is evident that an amplifier correctly designed, and operated under suitable conditions will show a linear relation between the input and output voltages. Since both the input voltage and output current, which is proportional to the output voltage, are measured by the thermo-junctions in cir-

cuits to be described later, the fidelity of the amplifier may be determined by a plot of input against output galvanometer deflections. This must give a straight line relation for all normal voltages applied to the amplifier.

General Experimental Procedure

In an experimental determination of the value of the electronic charge, the following method is employed:

The amplifier and shot-tube emitters are heated for about thirty minutes before actual observations begin. In this way the amplifier reaches a stable condition which can be maintained indefinitely. The plate circuit of the shot tube is then closed, giving a definite space current through the tube which is measured by ammeter A of Fig. 1. The shot voltage across the resistance AB is applied to the grid-filament circuit of the screen-grid amplifier, giving a deflection on the output galvanometer, G_0, which is proportional to the mean square voltage across AB. The shot circuit is then disconnected and a sine voltage is applied to the amplifier at its resonant frequency. This sine voltage is then varied until the deflection obtained with a definite space current in the shot circuit is reproduced. The magnitude of this sine voltage is the quantity V of the equation

$$\epsilon = V^2/2A\,i_0Z^2$$

as derived by Williams and Vincent.[2] Thus a measurable sine voltage at the resonant frequency of the amplifier is substituted for the actual voltage existing across AB due to the shot effect. Under ordinary conditions, this voltage is of the order of 25 micro-volts. Its value is obtained from the inductive drop along an inductance potentiometer.

In order to obtain the value of the charge of the electron from the equation of the shot effect, the quantities A and Z must be determined. A is the amplifier resonance area and is a constant for any series of measurements. The impedance Z of the shot circuit, measured between A and B, is a function of the space charge in the shot tube. The method of determining Z is discussed in the following section. Substitution of the quantities, i_0, V^2, A, Z^2 in the shot equation gives the charge of the electron. The space current and the accelerating voltage in the shot tube are varied, and conditions under which the true value of the electronic charge is given by the shot effect equation can be studied. Obviously, this method of investigation will show any abnormalities in the shot-effect characteristics of a given vacuum tube.

When thermionic currents of 300 microamperes or less are used in the shot tube, the deflection of the amplifier output galvanometer is small. Then the duplication of this deflection using only the inductance potentiometer results in large inaccuracies, since the I of $I\omega Ld$ is small. In order to minimize this error, the current is attenuated to a small fraction of its original value and this fraction is passed through the inductance potentiometer. The complete circuit used for the duplication of output galvanometer deflections due to the shot effect of the thermionic current in the tube S is shown in

[2] N. H. Williams and H. B. Vincent, Phys. Rev. **28**, 1250 (1926).

Fig. 2. With the use of the attenuator, high frequency voltages of the order of 10 microvolts can be measured with a probable error of one percent.

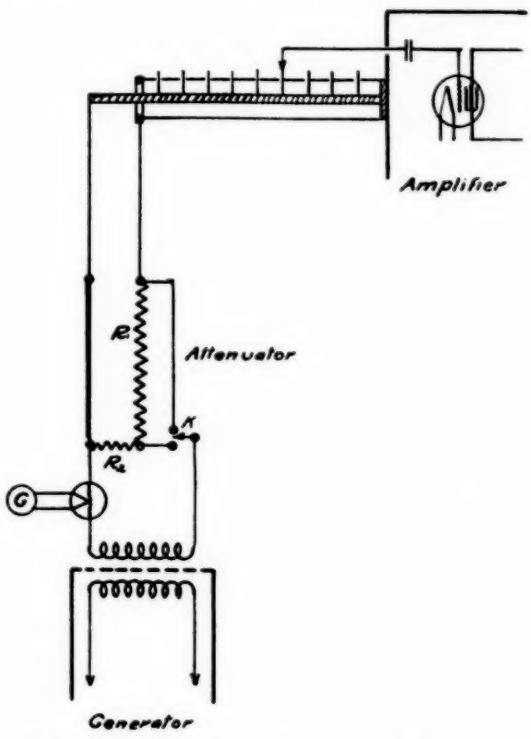

Fig. 2. Inductance potentiometer and attenuator.

Measurement of Impedance of the Shot Circuit

The impedance of the shot circuit involved in the equation

$$\epsilon = V^2/2A\,i_0Z^2$$

is that between the points A and B (Fig. 3) across which the voltage due to the fluctuations from the long time mean value of the space current is developed.

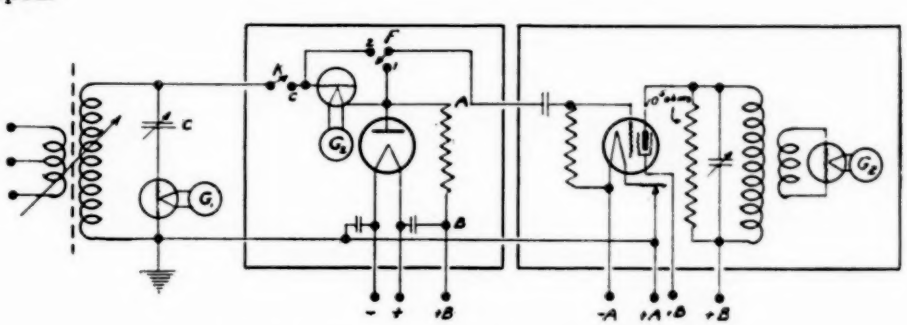

Fig. 3. Measurement of shot circuit impedance.

A process of measuring the impedance which is more direct than that of Williams and Huxford[3] and experimentally very simple has been developed. It was found that a coil and thermojunction system G_2, Fig. 3, coupled to the tuned plate circuit of the *first* screen-grid amplifier tube gives practically a linear response to the square of the high frequency voltage applied to the grid-filament circuit of the amplifier, if the tuned plate circuit is shunted by a resistance of the order of 100,000 ohms. In this way, the impedance of the plate circuit to the high frequency current, and the voltage amplification are lowered. We see that as the external impedance is made lower, say by shunting the tuned circuit with a high resistance, the voltage across it due to a given voltage applied to the grid filament circuit will decrease. The response of the first amplifier tube to various voltage inputs to the grid filament circuit is shown in curves I and II of Fig. 4.

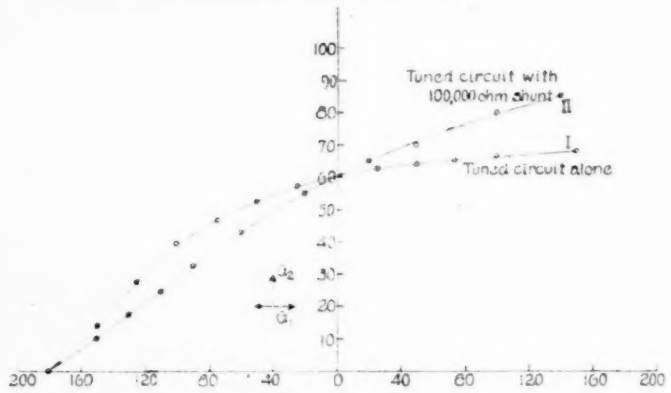

Fig. 4. Response of first amplifier tube as a high frequency voltmeter.

If any voltage at the resonant frequency of the amplifier is applied to the circuit at CB, Fig. 3, a current I_2 will flow through it. Also a deflection proportional to the square of the voltage between A and B will be observed on the galvanometer of G_2. The thermojunction measuring the current I_2 into the shot circuit is then shorted by key F, thus eliminating the voltage drop along it. The deflection previously obtained on the galvanometer of the system coupled to the plate circuit of the first amplifier tube is now duplicated by varying the current through the standard condenser, C. As the amplifier tube responds to the mean square voltage between A and B regardless of phase, it is evident that the voltage giving the same output deflection without the thermojunction G_2 in the circuit is now exactly the same as previously existed between A and B. The impedance of the circuit is then given directly by E'/I_2 where E' is the voltage applied directly between A and B for the observed deflection on G_2, and I_2 is the current read by the thermojunction system G_2. We have then, for the impedance of the shot circuit between the points A and B,

$$Z = I_1'/I_2C\omega.$$

[3] N. H. Williams and W. S. Huxford, Phys. Rev. **33**, 773–778, (1929).

Typical impedance characteristics of vacuum tubes, investigated under conditions of constant current at various voltages between the anode and cathode are shown in Fig. 5.

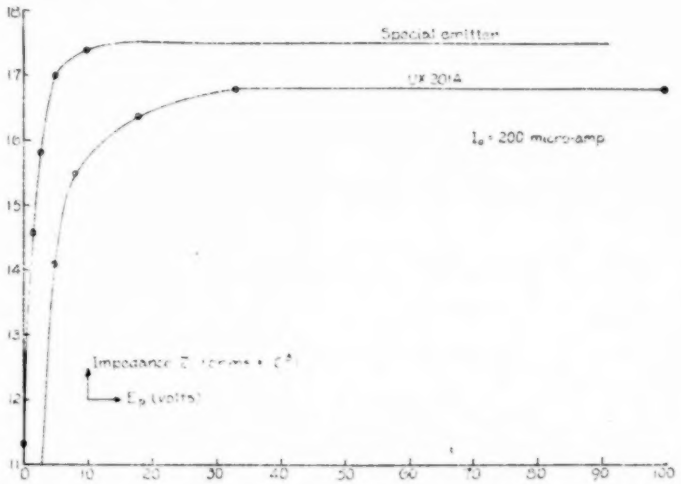

Fig. 5. Typical impedance characteristics of vacuum tubes.

Frequency Determination and Control

We see that

$$\epsilon = V^2/2A\,i_0Z^2$$

the shot effect equation, can be written in the form

$$\epsilon = \frac{I^2\omega^4L^2C^2}{2A\,i_0I_1^2/I_2^2}.$$

This follows from the fact that v, the high frequency voltage applied to the input circuit of the amplifier at its resonant frequency to give the same output deflections as the shot effect associated with a definite space current, is obtained from the inductance potentiometer and is given by

$$V = I\omega L.$$

Also the impedance Z is given by E/I_2 or as outlined in a previous section,

$$Z = I_1/I_2C\omega.$$

It is evident that oscillator frequency, entering the expression in the fourth power must be accurately determined and completely controlled.

Methods have been used whereby the frequency of the generator can be determined and held constant to one part in 100,000. A self-maintained tuning fork whose frequency may be varied from 800 to 1000 cycles per second is used as a primary standard of audio frequency. This is calibrated by a synchronous-motor clock which operates continuously when the fork is in operation. The audio frequency is introduced in the input circuit of a distor-

tion amplifier. By the use of several stages of amplification, harmonics of the audio frequency as high as 150 times the fundamental can be obtained. These are easily identified by a precision wave-meter and tuned circuits together with a heterodyne oscillator. By adjusting the frequency of the fork so as to obtain a zero beat of a harmonic with the fundamental frequency of a crystal-controlled or Hartley oscillator, the latter can be easily calibrated to an accuracy well within the needs of the procedure.

A crystal-controlled oscillator having a frequency of 117,034 cycles per second was calibrated by the procedure outlined and used as a high frequency standard. This was coupled to the Hartley oscillator used for the calibrating shot voltage and impedance measurements by means of pick-up coils and the amplified beat note was kept at one or two cycles per second. An audio frequency amplifier and dynamic loud speaker allowed the coupling between the crystal and the Hartley oscillator to be made so loose that there was no possibility of reaction of the circuits. The standard oscillator and audio amplifier were operated during actual observations so that any change in the frequency of the Hartley oscillator due to change of plate and filament voltage could immediately be noted and corrected.

In the determination of the resonance curve of the high frequency shot amplifier, the ratio of the amplification of a given voltage input at various frequencies to that at resonant frequency is measured. A convenient method of obtaining known frequencies in the pass band of the amplifier is that of selecting frequencies of the distortion amplifier in a suitable range. The Hartley oscillator is then adjusted to zero beat with these frequencies, whose separation is given immediately by the fundamental frequency of the tuning fork. Thus the resonance curve can be determined without the use of a wave-meter and with much greater precision and speed.

Measurement of the Electronic Charge from the Thermionic Emission of a Metal

Measurement of the shot effect of thermionic currents from a pure metal offers few complications and yields, under proper conditions, the accepted value of the electronic charge. The shot tubes used consist of a cylindrical collector plate of nickel, and a co-axial tungsten or thoriated tungsten emitter. The pressure in selected tubes is probably of the order of 10^{-6}mm of mercury. These tubes have been well outgassed and flashed with a getter. No evidence of ionization of the residual gas with the voltages employed has been found.

The shot effect associated with various anode currents from 100 to 6000 microamperes was studied. In all cases investigated, it may be said that the apparent charge of the electron, as given by the equation $\epsilon = V^2/2Ai_0Z^2$, agrees within the limits of experimental error with the values obtained by previous investigators, if the electron current leaving the cathode is temperature limited. That is, conditions in the experimental tube are such that all of the electrons leaving the emitter with a random distribution in time arrive at the collector in the same manner. Experimentally this condition can be

realized if the accelerating voltage across the tube is high and the space current is low. When an increase of the accelerating voltage causes no further increase in the space current, the electron stream is purely temperature-limited. Substitution of observed quantities under these conditions in the shot effect equation will give the accepted value of the electronic charge.

The space current for any given emitter temperature will be a function of the accelerating voltage up to the saturation region. When voltages higher than the saturation voltage are applied, little or no increase in the space current is observed. Thus a possible method of studying the shot effect associated with thermionic emission is that of holding the emitter at a constant temperature, and varying the voltage across the tube.

It is essential to distinguish very carefully between the value of "ϵ" obtained by the substitution of measured quantities in the equation of Williams and Vincent when the fundamental assumptions of Schottky's small-shot theory are fulfilled and values obtained when they obviously are not. Thus *only* at high accelerating potentials and low space currents, giving no first order space charge interaction of electrons, are we justified in using the equation as a measure of the electronic charge. At low voltages and high space-currents the equation merely gives values which are proportional to the voltage fluctuations occurring in the shot tube and circuit.

When the voltage between the emitter and the collector is low, the current is no longer temperature-limited and the space-charge density near the emitter may become very large. An electron emitted from the cathode is acted upon by a repulsive force due to the electrons in the space charge sheath. The redistribution in time due to such interaction is to make the fluctuations smaller than those existing with the same current at higher voltages. This we call space-charge depression. Under these conditions the deflections of the output galvanometer may become very small. An extensive investigation of space-charge depression of shot fluctuations is now in progress in this laboratory. Another effect, the fluctuation of the space charge itself, has been studied in the case of the electron emission from barium-strontium oxide coated cathodes. The shot effect of this emission has been investigated and the cause of certain abnormal defects has been determined.

Shot Effect of the Emission from Barium-Strontium Oxide Cathodes

During the summer of 1928, Williams and Huxford investigated the shot effect of electron currents from barium-strontium oxide emitters. The tube used contained a cylindrical quartz sleeve wound with platinum wire and then coated with a layer of barium-strontium carbonate mixture. The sleeve was surrounded by a co-axial cylinder as anode. Current passed through the platinum wire heats the emitter. The tube used had a geometry identical with the Kunsman emitter of positive ions described by Huxford.[4] It was hoped that the results obtained with the Kunsman emitter of positive ions

[4] W. S. Huxford, Dissertation, University of Michigan, 1928.

and an emitter of electrons such as barium-strontium oxide would allow calculation of the influence of the mass of the carrier on the space charge.

This tube was sealed onto a high vacuum system and baked and outgassed with the induction furnace until the vacuum could be maintained at 10^{-6}mm of mercury. With the vacuum system in operation the shot effect characteristics of the two were studied. The ordinary shot effect curves for an electron emitter were expected. Actually it was found that the shot effect behaved very abnormally under certain conditions of space charge. The shot-effect characteristics are graphically shown in Fig. 6. Four complete shot-characteristic curves were taken with this tube. The tube was on the pumps continually and the emitter was being heated except for a very short time between curves II and III when the system was brought to atmospherie

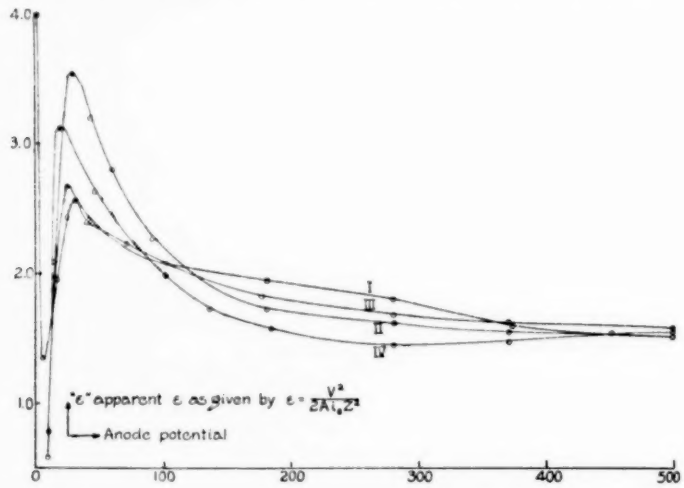

Fig. 6. Shot effect of electrons from barium oxide. $I_0 = 200$ microamps.

pressure for adjustment. We notice the characteristic space-charge depression at very low accelerating voltages on the tube. As the voltage on the tube is increased, v^2 increases very rapidly, reaches a maximum, and falls rapidly with a further increase of accelerating potential. From then on, with further increase of accelerating potential the behavior is similar to that in a metallic emitter. At high accelerating voltages, the value of v^2 is such as to give values of the electronic charge which agree with the accepted value within the limits of experimental error. Thus, since there is no possibility of gas ionization, and the abnormally high fluctuations disappear with high accelerating potentials, when space charge is obliterated, it appears that there exists an agency which operates on the space charge in such a manner that large, mean-square fluctuations are produced. It should be noted that there is a very good correlation between the length of time that the emitter has been heated, or activated, and the magnitude of the space-charge peak. In the following sections the cause of these fluctuations will be discussed and experimentally verified by an independent method.

In order to obtain more data on the shot effect with oxide coated emitters, commercial tubes of the UY-227 type were studied. These are the familiar indirectly heated barium-strontium oxide cathode type, designed for alternating current operation. During the process of activation the barium and strontium carbonates break down into the oxides, with the evolution of carbon dioxide. Thus the gas content of a tube of the 227 type is higher in general than that of a tube employing a pure metal emitter. In every case, the shot-fluctuation voltages at high accelerating potentials are from three to four times normal value. The deflection of the high frequency amplifier output galvanometer, which is proportional to v^2, is not steady but may fluctuate from its mean position by as much as 25 percent. This is a good indication of the presence of gas in the tube.

If an evacuating system is sealed on to any of the commercial tubes studied, and the tube is well outgassed and held on the vacuum system at a pressure of 10^{-6}mm of mercury, a curve of "ϵ" against the accelerating voltage using a constant space current is found which has all of the essential characteristics of the oxide emitter described by Williams and Huxford. Thus we can conclude that even a small amount of gas in a shot tube will introduce fluctuations over and above the normal fluctuations in purely thermionic emission. This action of the gas is probably due to the positive ions and electrons obtained by ionization. In order to correlate the effects in the space charge region, all tubes subsequently studied were investigated under a high vacuum.

Activation of the Emitter and Shot Effect in the Space Charge Region

Commercial tubes whose emitters were unactivated were fitted with a five-millimeter-diameter evacuating tube and were sealed on to the evacuating system to obtain a high pumping speed. The pressure was brought down to 10^{-5}mm of mercury and the tube was then baked for 2 or 3 hours with an electric furnace at a temperature of 350–400°C, with the emitter operated at half-voltage. Large quantities of gas were evolved in the process. Toward the end of the treatment, the emitter was operated at normal temperature. The metal parts of the tube were then outgassed with an induction furnace. The emission from the cathode was measured by applying a low voltage between the cathode and the collector plate. By overheating the emitter for a short time and then bringing it back to its normal operating temperature, it was found that the emission materially improves. An application of the induction furnace in the early stages of activation causes the emission to decrease temporarily.

A detailed study shows that a very good correlation exists between the shot effect associated with the emission from an oxide cathode and the degree of activation of the cathode. The shot effect characteristics were determined under conditions of constant anode current for various anode voltages at successive stages in the activation of the emitter. They are represented in the curves of Fig. 7. In the case of curve I, we see the begin-

ning of a small peak in the space charge region. The high values of v^2 at higher voltages are obviously due to gas ionization as is shown by the sharp upward trend beyond 120 volts. A comparison of the curves shows that the magnitude of the peak in the space-charge region increases with the length of time the emitter has been heated. Curve III shows complete stability even at high voltages. A study of the activation curves of the emitter shows an increase in the reverse current as the emitter becomes more activated. This indicates that positive ion emission increases. These results show that the

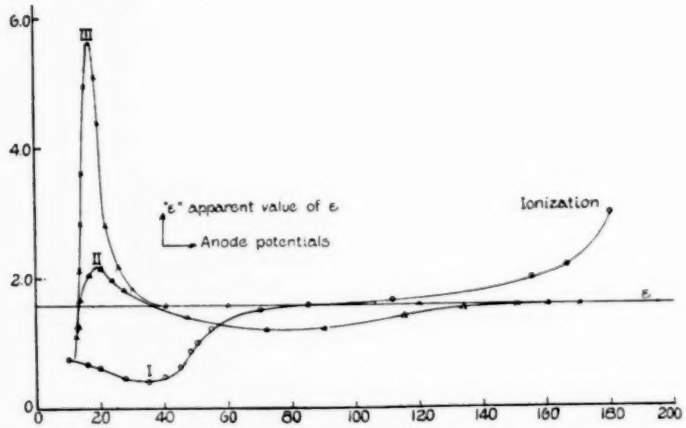

Fig. 7. Shot effect of electrons from barium oxide. $I_0 = 200$ microamps

fundamental cause of the abnormal fluctuations in the space charge region is the activity of positive ions emitted from the oxide cathode into the space charge region.

A study of the activation of oxide emitters shows that the electron emission increases with the length of time the cathode has been heated. If the cathode is overheated, the electron emission rapidly improves to a maximum value and then slowly decreases. An oxide emitter may be completely activated merely by a prolonged heat treatment, gas-ion bombardment not being at all necessary to the process. At the time of the decrease of electron emission, measurable amounts of reverse current may be detected between the emitter and the plate if a negative potential is applied to the latter. By a high overheat it is possible to get 10 microamperes or more of reverse current. A more critical investigation shows that the reverse current does not consist entirely of positive ions in all cases. For one commercial tube, only 10 percent of the total reverse current was found to consist of positive ions. The remainder is due to photo-emission of electrons from the plate and grid elements by the radiation from the cathode. This has been verified by illuminating the elements with light from an external source, keeping the barium-strontium emitter cold. The magnitude of the current thus obtained is of the same order as with the cathode hot. If the plate and grid are negative with respect to the oxide emitter and they are photo-active, we are unable to

distinguish between positive ions going to them from the oxide and photoelectrons going in the opposite direction. The photoactivity of the grid and plate is very probably due to the evaporation of barium or barium oxide from the cathode and a recondensation on these elements so as to give a surface with a low photoelectric work function.

The problem of identifying positive ions in the emission from barium-strontium cathodes was solved by the use of the familiar magnetron method of Hull.[5] He has shown that in the case of co-axial cylindrical emitter and collector and a uniform magnetic field applied along the axis of the system, the magnetic field required to prevent electrons or ions emitted by the inner cylinder from reaching the outer collector is given by

$$H = \left(\frac{8m}{e}\right)^{1/2} \frac{V^{1/2}}{R}$$

where m is the mass of the electron or ion, e is the charge of the electron or ion, V is the accelerating potential between the cylinders and R is the radius of the outer collecting cylinder. This assumes that the ratio of the radius of the inner cylinder to that of the outer cylinder is small. We see immediately that for a given voltage, the magnetic field required to prevent a barium or strontium ion from reaching the plate will be about 500 times that required for an electron. For

$$\frac{H_p}{H_e} = \left(\frac{m_p}{m_e}\right)^{1/2}.$$

A special tube containing a unipotential oxide-coated emitter and a nearly co-axial collecting cylinder of molybdenum was constructed. The radius of the collector was large compared to that of the emitter. The plate was therefore located so far from the emitter that recondensation and consequent photo-activity was very small. A solenoid consisting of several thousand turns of copper wire, layer wound, was so constructed that the special tube could be placed in the core with the collector and emitter axes parallel to the magnetic field produced by passing a direct current through the solenoid. Thus the above equation for the motion of the electrons or positive ions under the influence of the electric and magnetic field applies in all detail.

A potential of 22 volts positive with respect to the emitter was applied to the collector. A reflecting galvanometer of sensitivity 10^{-8} amperes was used to measure the space current. When the magnetic field was applied, the current dropped to 20 percent of its original value. It did not drop to a smaller value probably due to a lack of complete symmetry in the arrangement of the emitter and collector. This is the behavior to be expected with electrons. More elaborate experiments might serve to detect the presence of negative oxygen ions in the emission. The potentials were then reversed and the emitter heated until the same space current was again obtained. Application

[5] A. W. Hull, Phys. Rev. **18**, 31 (1921).

of a magnetic field now caused less than 0.5 percent decrease in the space current. This can be taken as conclusive evidence that heavy ions are emitted from oxide emitters. Evidence from photoelectric long wave limits points to these ions being barium or strontium. Absolute determination of the magnetic field would allow the mass of the ions to be determined. However, a mass spectograph analysis would perhaps be easier to carry out and would yield information about the relative proportions of the various ions present.

A report by Glass[6] on the variation in emission of oxide filaments assumes that all of the reverse current is composed of positive ions. Obviously he has neglected the possibility of photo-emission from the grid and plate. This in commercial tubes is of the same order as the emission of positive thermions.

Shot Effect at Constant Emitter Temperature

In order to obtain the preceding shot-effect curves with constant space current for a range of accelerating voltages it is necessary to vary the temperature of the emitter over a rather wide range. This raises a question as to whether the abnormal fluctuations may not be due to a property of the emitting surface at a certain temperature. To test this point, characteristics of the shot effect were obtained under conditions of constant emitter temperature. The power input to the cathode was held constant at a convenient value, and the fluctuations as observed by the output galvanometer of the high frequency amplifier were studied as a function of the space current as the accelerating potential was varied. The space-current characteristic and the fluctuations observed are plotted against accelerating voltage in Fig. 8. We notice first the typical lack of saturation of the oxide emitter. Here again we have the familiar space-charge depression of fluctuations at very low voltages, then a space-charge peak at higher accelerating field, and finally a portion where the fluctuations are directly proportional to the space current. This is shown by the space current and fluctuation curves becoming parallel. Absolute values of Z and V^2 under these bonditions will yield the true value of the electronic charge. Thus it is evident that the peak is not due to changes in the structure of the emitter with temperature, but is a function of space charge. A series of curves taken with various power inputs to the cathode shows that the peak moves toward higher voltages with increased emission.

At a critical value of space charge, a positive ion emitted from the cathode travels in the direction of the potential minimum. By virtue of its large mass and consequent low mobility, it can release a large number of electrons from space charge. Langmuir[7] has shown that a single ion can release several hundred electrons from space charge. The random emission of positive ions from the cathode and their passage through the space charge region causes large fluctuations in the space charge, producing an abnormally high V^2 across the shot circuit. It is natural to suppose that the magnitude of

[6] Myron S. Glass, Phys. Rev. **28,** 521 (1926).
[7] Irving Langmuir, Phys. Rev. **33,** 954 (1929)

the peak will be a function of the amplifier frequency. Peaks have been found at audio frequencies with oxide coated commercial tubes in this laboratory by Mr. Thatcher. The frequency characteristics of the phenomenon are now

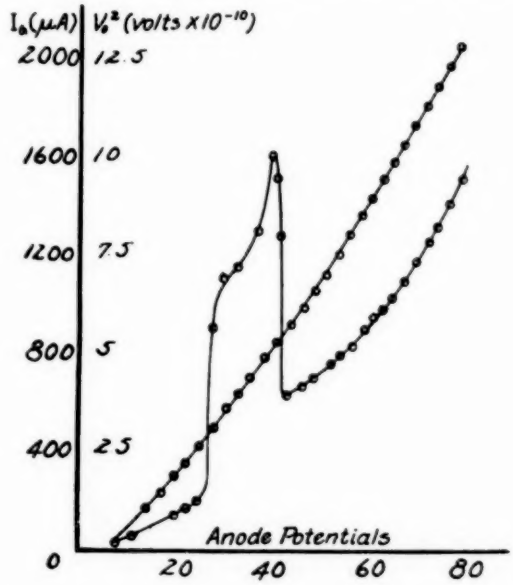

Fig. 8. Shot effect with barium oxide emitter at constant temperature. $I_f = 1.71$ amp., $E_f = 2.66$ volts.

under investigation. It is to be observed that when space charge is obliterated by the use of high accelerating potentials, the mechanism of the fluctuation

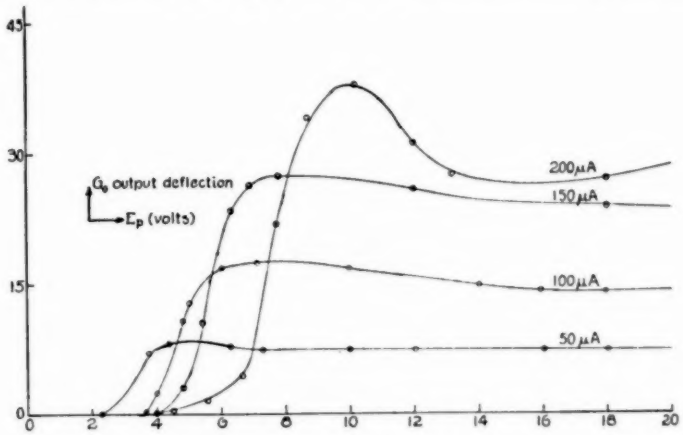

Fig. 9. Position of space charge shot effect peak for various I_b values. Barium oxide emitter.

no longer exists. Positive ions emitted from the cathode are unable to travel in the tube because of the adverse field, and there are no space charge electrons to be released. Therefore, under these conditions, the true value of

the electronic charge is obtained. As the space current becomes smaller and smaller we would expect the magnitude of the space charge peak to decrease. A series of four curves given in Fig. 9 taken with four constant space currents at various accelerating voltages shows the dependence on current. The results are of the same nature as Johnson reports with the flicker effect at low frequencies. If the space current is low enough, normal fluctuations are obtained.

An Experimental Verification of the Space Charge Effect

Since the abnormal behavior of the fluctuation voltage is due only to positive ions in the presence of an electron space charge, an attempt was made to reproduce artificially the conditions believed to exist with an oxide emitter. A vacuum tube containing two independent emitters mounted very close together and surrounded by a cylindrical collector plate was constructed. The first emitter is a pure tungsten wire which emits only

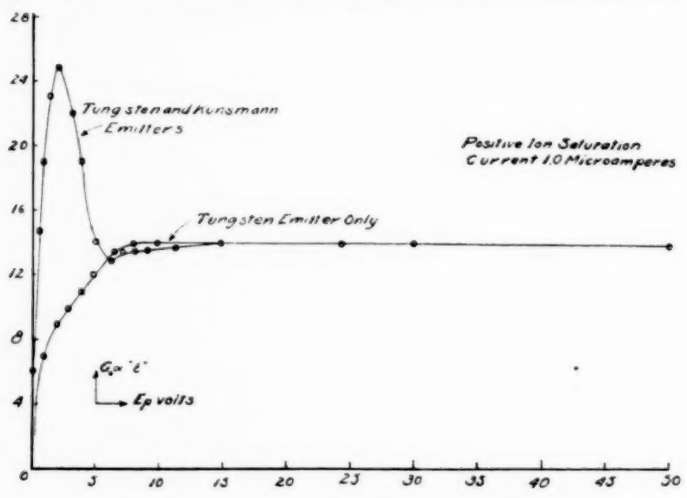

Fig. 10. Shot effect for special tube. $I_0 = 150$ microamps.

electrons when heated. The second is a Kunsman oxide emitter. This, at a temperature of about 900°C, gives off positive potassium ions and a small number of electrons. The ratio of the positive ion to the electron emission is about 1000 to 1 at 900°C. If the shot effect of each emitter is studied separately, the results obtained are normal. That is, at low voltages, the fluctuation voltage is very low due to the effect of space charge on the random distribution in time of the emitted ions or electrons. However, if the two emitters are operated simultaneously, positive ions emitted by the Kunsman emitter, will, at low voltages across the tube, travel into the electron space charge region. Space-charge density can be controlled by the temperature of the tungsten emitter, and by the voltage between the emitters and the anode. A typical curve for this tube operated under conditions simulating those believed to exist in an oxide-emitter tube is given in Fig. 10. A curve for the tungsten emitter alone is also included. The

space current in the tube using first only the tungsten emitter, and then the combination of tungsten and Kunsman emitters, was held constant at 150 microamperes. The general characteristics of the shot effect are those obtained with the oxide coated emitter. It is interesting to note that as soon as space charge is removed, the peak disappears.

Thus it has been shown that the abnormally high shot voltage observed in the space charge region when an oxide emitter is used can be duplicated by the interaction of positive ions from an independent emitter with an electronic space charge. The thermions from a Kunsman[8] emitter have been identified by the mass spectograph as positive potassium ions. The abnormally high shot effect observed disappears when the source of positive ions has been cut off, and also disappears at high accelerating potentials. Therefore, we have conclusive evidence that the abnormal shot effect is due to positive ions moving through space charge.

Shot Effect of Evaporating Surface Films

During the study of the shot effect, a special tube containing a barium oxide and a tungsten emitter mounted close to one another was used. This tube was very highly evacuated and thoroughly outgassed, and then sealed off. The oxide emitter was thoroughly activated during the process of evacuation. No trace of residual gas was detected with the voltages applied to the tube. The tungsten emitter alone gave normal shot effect. If, however, the barium oxide emitter was operated for a short time with the tungsten cold, and then the tungsten emitter was suddenly brought to full brilliancy, the shot-output galvanometer gave a deflection of the order of 3000 mm. This decreased exponentially with the time to the normal value of 30 mm corresponding to the shot effect associated with the space current used. On the basis of Becker's[9] work with oxide emitters, it is probable that some barium of the surface layer of the activated emitter evaporates from the oxide emitter and condenses on the tungsten emitter. On bringing this tungsten emitter to its operating temperatures suddenly, the barium evaporates in the form of barium ions which interact with the space charge in the usual manner. No such surge was noticed with a high accelerating voltage across the tube. The same phenomenon was noticed with the Kunsman tungsten emitter tube.

Absolutely no surge is noticed on bringing the tungsten emitter to full brilliancy after it has been thoroughly cleaned of this layer by operating at a high temperature for three or four minutes. The decay of the surge due to a layer formed by evaporation of either barium or barium oxide onto the tungsten emitter can be controlled by varying the operating temperature. It appears that the process of this film leaving the surface is quite the same as occurs in the deactivation of a thoriated tungsten emitter. No evidence of such a surge was found using a thoriated tungsten emitter brought suddenly to a temperature where the thorium leaves the tungsten and leaves it deactivated. This can probably be interpreted to mean that thorium leaves a thoriated tungsten emitter in a neutral state and not as an ion.

[8] N. A. Barton, C. P. Harnwell, C. H. Kunsman, Phys. Rev. **27**, 739–746 (1926).
[9] Joseph A. Becker, Phys. Rev. **34**, 1323 (1929).

A PHOTOGRAPHIC METHOD OF DETERMINING ATOMIC STRUCTURE FACTORS

By Darol K. Froman
Ryerson Physical Laboratory University of Chicago

(Received August 27, 1930)

Abstract

The intensities of x-rays reflected from powdered crystals of magnesium oxide and potassium chloride were measured photographically. It was found that this method made possible the measurement of somewhat higher orders of reflection from powdered crystals than have been determined by the ionization method. The radial electron distribution for each of the atoms was determined and the results indicate that both compounds form polar crystals.

Introduction

ELECTRON distributions and atomic structure factors have been determined by many experimenters from measurements of the intensity of monochromatic x-rays reflected by the various atomic planes of a powdered crystal mass. It has been shown[1] that the electron distribution in a crystal can be represented by a Fourier series, each term of which depends on the intensity of the corresponding order of reflection. In order to evaluate as many terms of this series as possible, and thus to determine the electron distribution with precision, it is important to measure the higher orders of reflection. Since the intensities in the higher orders are often so small that ionization measurements are inaccurate, it was thought that the cumulative property of the photographic film might be used to obtain better measurements in this region.

Apparatus and Experimental Procedure

A schematic arrangment of the apparatus is shown in Fig. 1. A cylindrical lead camera, C, was supported on an insulating stand about one inch from a Coolidge x-ray tube with an Mo target. The middle portion of the tube was covered with tin foil, which was connected to the camera to prevent sparks puncturing the glass. X-rays from the target fell on a calcite crystal, K_1, which was so oriented that the K_α line was reflected through the slits in the camera to the sample of powdered crystal, S. A photographic film, F_1, was bent to fit the inside of the camera, and a zirconium oxide filter placed just in front of it. The main x-ray beam, after transmission through the sample, was caught in a lead shield, L. Sometimes the crystal K_1 was removed and the direct rays allowed to fall on the sample, only the filter being used to limit the wave-lengths of the x-rays. In this case the intensity was increased greatly.

[1] A. H. Compton, "X-rays and Electrons," p. 164.

The samples were powdered crystal cylinders about 1 mm in diameter and 6 mm long. The powder was passed through a 200 mesh screen and was fine enough to eliminate primary extinction.[2] An emulsion of the powder in a little household cement and amyl acetate was made, and the cylinders were formed by extruding the mixture through a small circular aperture. These cylinders, although containing only about eight percent by weight of celluloid, were quite stable.

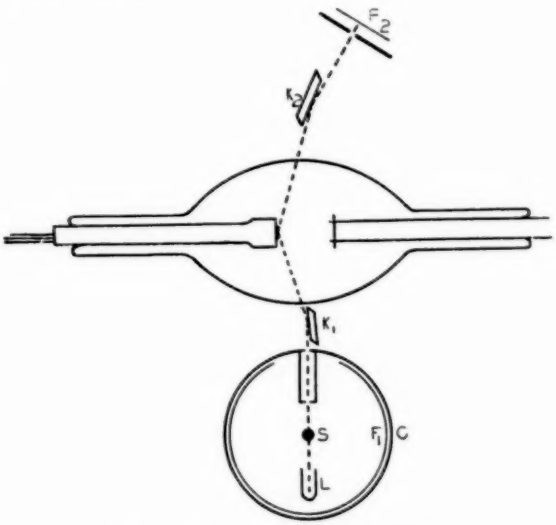

Fig. 1. Arrangement of apparatus.

During an exposure the K_α line from another crystal, K_2, was allowed to fall on a second film, F_2. A series of exposures with different exposure times was taken giving lines whose relative intensities were known, since it was assumed that the effect on the film was a function of the product of the intensity and the time of exposure. Both films were always cut from the same piece, developed together and given identical treatment. The films were examined with a Moll microphotometer and the galvanometer deflections measured for the various lines. The known intensities of the lines on film F_2 provided a calibration curve from which the relative intensity of any point on film F_1 could be determined. Fig. 2 shows a typical calibration curve obtained in this way. The ordinates are proportional to the exposure times and thus they represent relative intensities. A plot of intensity, determined in this way, against θ always showed that the powdered crystal lines were very nearly triangular and that their widths were constant. Thus the intensity of the peak was proportional to the integrated intensity, P_s, of the line and it was necessary to measure only this peak intensity. Fig. 3 shows a microphotometer trace of a typical film of the reflections from KCl. The line *D. B.* is the zero position of the galvanometer. An absolute determination of the intensity of one line was made by a photographic comparison with

[2] R. J. Havighurst, Phys. Rev. **28,** 869 (1926).

the known reflections of NaCl. In this case the lines were of different widths and it was necessary to take the area under the intensity curve for the integrated intensity.

Fig. 2. Intensity calibration curve.

The structure factors were computed from the relation:[3]

$$F^2 = AP_s \sin^2\theta \cos\theta / p(1 + \cos^2 2\theta) \qquad (1)$$

in which P_s is the power in the reflected beam, θ the grazing angle of reflection and p the number of planes per unit cell contributing to reflection at angle θ. A represents a group of constants which were determined from the comparison with NaCl.

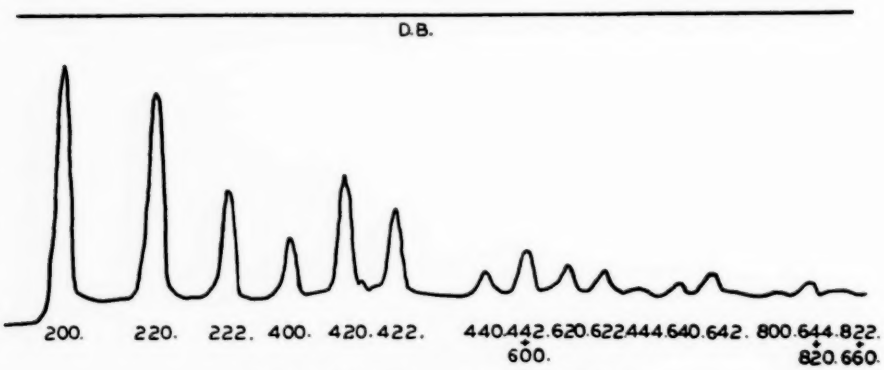

Fig. 3. Microphotometer trace of film.

[3] A. H. Compton, "X rays and Electrons," p. 131.

Results

Measured values of the relative intensities, P_s, and the corresponding structure factors, F, are given in Tables I and II for MgO and KCl respectively.

Table I. *Structure factors of MgO.*

Line	sin θ	P_s	F
111	0.1464	21.8	2.46
200	0.1691	353.0	13.25
220	0.2390	199.0	10.15
311	0.2804	22.1	2.85
222	0.2929	55.1	8.19
400	0.3380	21.2	6.41
331	0.3684	9.16	2.50
420	0.3780	46.8	5.83
422	0.4140	27.5	4.99
511+333	0.4392	4.25	1.81
440	0.4782	5.25	3.68
531	0.5000	1.40	0.997
442+600	0.5071	11.2	3.66
620	0.5344	5.66	3.07
533	0.5542	1.00	1.36
622	0.5606	4.80	3.03
444	0.5856	1.64	3.22
711+551	0.6036	0.8	0.949
640	0.6095	3.54	2.85
642	0.6324	6.17	2.77
731+553	0.6492	0.955	0.91
800	0.6762	0.658	2.71
733	0.6918	0.451	1.14
820+644	0.6970	3.68	2.31
822+660	0.7172	2.56	2.26
555	0.730	0.155	1.18
662	0.745	1.46	2.11
840	0.755	1.36	2.03
911+753	0.769	0.655	0.815
842	0.773	2.12	1.80
664	0.793	1.08	1.80
931	0.805	0.25	0.608
844	0.827	1.12	1.78
933+755+771	0.840	1.23	1.06
10,00+860	0.845	0.605	1.14
10,20+862	0.862	2.38	1.42
951	0.875	1.58	1.38
10,22+666	0.878	1.66	1.72
953	0.905	1.09	1.06
10,40+864	0.907	0.977	0.815
1042	0.924	0.769	0.835
11,11+775	0.936	0.396	0.570
880	0.956	0.250	0.815
882	0.962	0.818	1.00
11,31+955	0.966	0.256	0.313
1044	0.969	0.733	0.890

spectively. The probable errors in the intensities are about five percent in the highest values and about twelve percent in the smallest. Figs. 4 and 5 show the structure factors plotted against sin θ for MgO and KCl respectively. No odd order reflections were obtained from the latter crystal. The intensities of several lines of high order of reflection which have not been measured by the ionization method have been determined. For example ionization measurements on MgO have not been carried past $(\sin\theta)/\lambda = 1$, whereas

TABLE II. *Structure factors of KCl*

Line	sin θ	P_s	F
200	0.1131	680.	12.08
220	0.1599	393.0	9.33
222	0.1959	127.0	8.04
400	0.2261	57.5	7.26
420	0.2529	144.0	6.50
422	0.2770	87.7	5.60
440	0.3199	19.3	4.36
600+442	0.3392	34.5	4.36
620	0.3575	19.8	3.56
622	0.3750	17.1	3.50
444	0.3918	5.07	3.48
640	0.4078	9.60	2.90
642	0.4231	14.5	2.66
820+644	0.4663	11.1	2.60
822+660	0.4798	3.8	1.82
662	0.4984	1.83	1.62
840	0.5051	2.57	1.95
842	0.5173	3.62	1.34
664	0.5307	4.26	2.10
844	0.5534	2.14	1.54
10,20+862	0.5769	2.05	0.90
10,22+666	0.5876	1.01	0.96

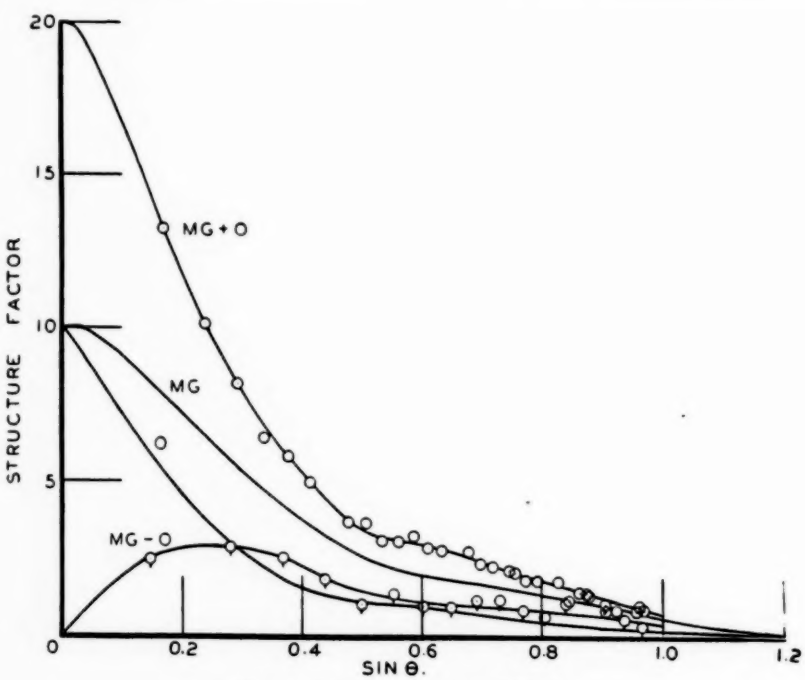

Fig. 4. Structure factors of MgO.

measurements were made with the photographic method as far out as $(\sin\theta)/\lambda = 1.35$.

The radial electron distribution for the different atoms,[4]

[4] A. H. Compton, "X-rays and Electrons," p. 164.

$$U = (8\pi r/D^2) \sum_{n=1}^{\infty} nF_n \sin(2\pi nr/D) \quad (2)$$

where n is the order of reflection and F_n the corresponding structure factor, was determined by a mechanical synthesis. The synthesis was made with Michelson's[5] harmonic analyser which is designed to analyse a curve into its first eighty Fourier components. To synthesize, it was necessary only to displace the ends of push rods distances proportional to the corresponding coefficients and, upon turning a crank, the result was traced out. Friction of

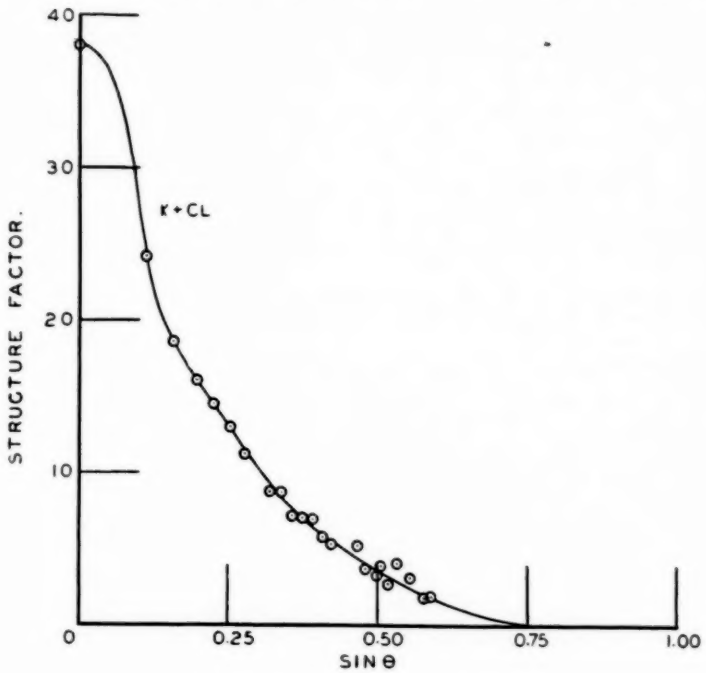

Fig. 5. Structure factors of KCl.

the pen point caused some error, so instead of a pen a slit was attached to the tracing arm which moved at right angles to its length. Back of this slit another stationary slit was placed at right angles to the first. Sensitized paper was used on the movable table and the curve traced by means of a beam of light passing through the crossed slits. Arbitrary grating spaces were chosen and the values of nF_n were set on the synthesizer. It will be seen from Eq. (2) that the result was a curve for U/r. A typical example of the analyzer trace is given in Fig. 6, which shows U/r for oxygen. The curve was obtained by multiplying the ordinates of this curve by their respective abscissas. Arbitrary grating spaces of 4.82 and 7.10A were chosen for MgO and KCl respectively. Somewhat different results for Mg and O might be expected in the U curves for different extrapolations of the odd order

[5] A. A. Michelson and S. W. Stratton, Amer. Journ. Sci. **5**, 1 (1898).

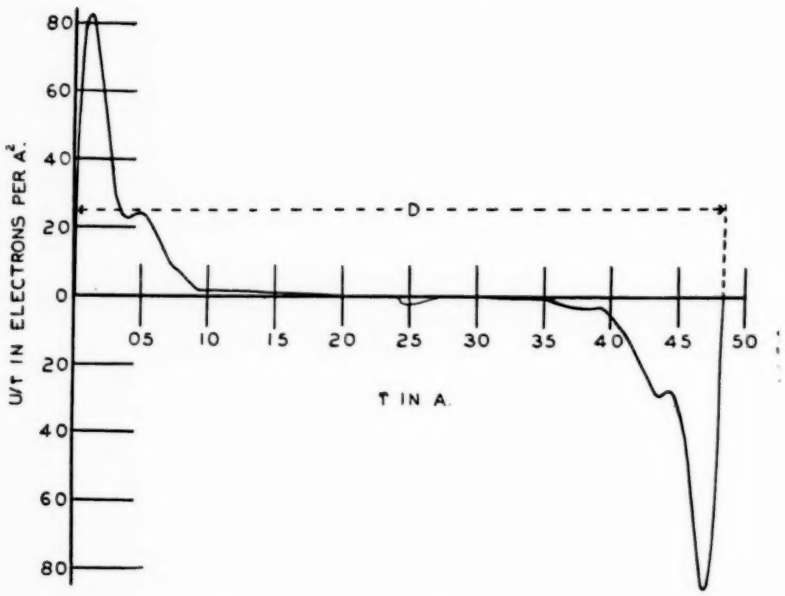

Fig. 6. Harmonic analyzer trace.

structure factor curve. Fig. 7, curve 1, shows the electron distribution of oxygen when the odd order structure factor curve is extrapolated to zero for

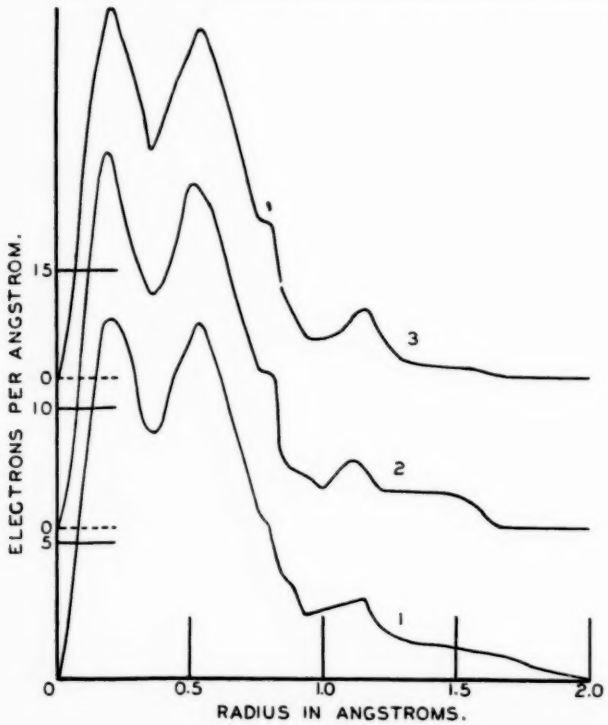

Fig. 7. Electron distribution of oxygen.

sin $\theta=0$. Curve 2 shows U for extrapolation to $F=2$ and curve 3 for extrapolation to $F=4$ at sin $\theta=0$. The three curves will be seen to be very similar. The area under such a curve represents the total number of electrons

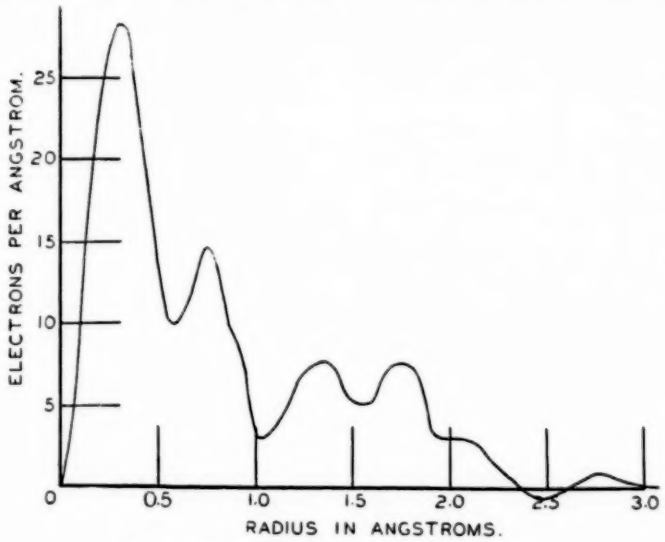

Fig. 8. Electron distribution of magnesium.

in the atom. The area under curve 1 is equivalent to 9.4 electrons and the areas under curves 2 and 3 are slightly greater than this, but the differences are not as great as 1 and 2 electrons respectively. Fig. 8 gives U for Mg for

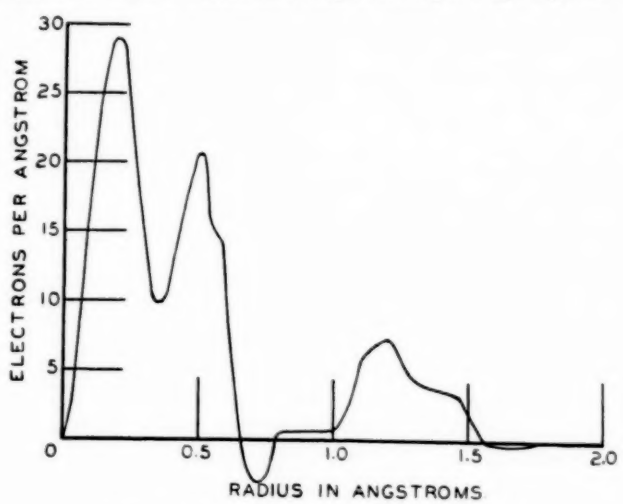

Fig. 9. Electron distribution for K and Cl.

extrapolation to zero, and Fig. 9 shows U for K an Cl, which, since the odd orders do not appear, cannot be distinguished by this method. Structure factors corresponding to reflections of different orders from the (111) planes were used throughout the analysis.

The total number of electrons per atom as determined from[6]

$$Z = -2\sum_{n=1}^{\infty}(-1)^n F_n \tag{3}$$

was found to be 9.30 for oxygen, 10.32 for magnesium and 18.0 for both chlorine and potassium. This indicates polar crystals probably consisting of $Mg^{++}O^{--}$ and $K^{+}Cl^{-}$. The results for MgO are in fair agreement with those obtained by Wollan.[7] The important differences are that the structure factor for the (111) plane was found to be somewhat less than for the (311) plane, Wollan finding them to be about equal; and that the structure factor curves are slightly higher than Wollan's for large values of sin θ. If the (111) factor is less than the (311) factor it is an indication that the odd order curve, (Fig. 4) should be extrapolated to zero. James and Brindley[8] have measured the structure factors for KCl but it is a little difficult to compare their results with those reported here, since they do not give their original data and have applied some unknown corrections.

In conclusion the writer wishes to express his appreciation to Professor A. H. Compton, who suggested this problem, for his many very valuable suggestions during the course of the work.

[6] A. H. Compton, "X-rays and Electrons," p. 165.
[7] E. O. Wollan, Phys. Rev. **35,** 1019 (1930).
[8] R. W. James and G. W. Brindley, Proc. Roy. Soc. **121,** 155 (1928).

A NOTE ON THE EXTRAPOLATION OF ATOMIC STRUCTURE FACTOR CURVES

By Darol K. Froman
Ryerson Physical Laboratory, University of Chicago

(Received August 27 1930)

Abstract

An approximate extrapolation formula for atomic structure factors of high order has been deduced from the form of the electron distributions indicated by the wave equation. The result is compared with the structure factors determined from Hartree's[1] electron distribution for Na^+. The agreement is good enough to warrant the use of the formula in extrapolating experimentally determined structure factor curves. It is shown that an analagous treatment can be applied to the "S" curves obtained from the scattering of x-rays by gases.

Extrapolated Structure Factors

THE structure factors of the first few orders of reflection can be determined without great difficulty, and a rational method of extrapolation of the structure factor curve to high orders may be valuable.

The radial electron distribution $U(r)$, and the nth order structure factor, F_n, are related[2] by Eq. (1).

$$U(r) = (8\pi r/D^2)\sum_{n=1}^{\infty} nF_n \sin(2\pi nr/D) \tag{1}$$

where D is the first order grating space. Multiplying by $\sin(2\pi mr/D)dr$ and integrating from 0 to $D/2$

$$\int_0^{D/2} \frac{U(r)}{r}\sin\frac{2\pi mr}{D}dr = \frac{8\pi}{D^2}\int_0^{D/2}\sum_{n=1}^{\infty} nF_n \sin\frac{2\pi mr}{D}\sin\frac{2\pi mr}{D}dr$$

$$= \frac{8\pi}{D^2}\sum_{n=1}^{\infty} nF_n \int_0^{D/2}\sin\frac{2\pi nr}{D}\sin\frac{2\pi mr}{D}dr$$

$$= O \text{ for } m \neq n$$

$$= \frac{8\pi}{D^2} mF_m D/4 \text{ for } m = n.$$

Putting $m = n$ and solving for F_n,

$$F_n = (D/2\pi n)\int_0^{D/2}\frac{U(r)}{r}\sin\frac{2\pi nr}{D}dr. \tag{2}$$

The Schrödinger equation for the hydrogen-like atom

[1] D. R. Hartree, Proc. Camb. Phil. Soc. **24**, 189 (1928).
[2] A. H. Compton, "X-rays and Electron," p. 164.

$$\Delta^2\Psi + (8\pi^2 m/h^2)(E + Ze^2/r)\Psi = 0 \tag{3}$$

has a solution separable in the polar coordinates, r, θ and ϕ,

$$\Psi = R(r)P_l{}^m(\cos\theta)e^{im\phi} \tag{4}$$

where m is the magnetic quantum number, l the azimuthal quantum number minus 1 and $p_l{}^m$ is the Legendre polynomial of degree l and order m.

$\Psi\Psi^*$ when suitably normalized, represents the density of electricity at the point (r, θ, ϕ) and averaging over the sphere of radius r,

$\overline{\Psi\Psi}^* = a_{lm}R^2$ where a_{lm} is the average "square" of the angle functions.

Substituting the assumed solution (4) in equation (3) an equation in R and r is obtained which has as its solution[3]

$$R(r) = e^{-\rho/2}\rho^l \sum_{v=0}^{n_r} b_v\rho^v$$

where $\rho = 2r/r_0 = 2r/(-h^2/8mE)^{\frac{1}{2}}$, $n_r = n-(l+1)$, n being the total quantum number, and $b =$

$$\frac{(v+l+1)(v+l)+2(v+l+1)-l(l+1)}{v+l+1-n} b_{v+1}$$

But

$$\begin{aligned} U(r) &= 4\pi r^2\overline{\Psi\Psi}^* \\ &= 4\pi r^2 a_{lm}e^{-\rho}\left[\sum_{v=0}^{n_r} b_v\rho^{v+l}\right]^2 \\ &= 4\pi r^2 a_{lm}e^{-\beta r}\left[\sum_{v=0}^{n_r} D_v r^{v+l}\right]^2 \end{aligned} \tag{5}$$

where $\beta = 2/r_0$ and $D_v = (2/r_0)^{v+l}b_v$

Since the number of nodes in $R(r)$ is not affected by screening, let us assume that the general shape of the electric density distribution curve for any one electron in an atom or ion is given by an equation similar to (5). However, since $R(r)$ will not be identical for electrons in corresponding orbits of different atoms, the recursion formula for the D's will not be assumed to hold.

Then for any atom or ion with N electrons

$$U(r) = \sum_{i=1}^{N} \alpha_{l_i m_i i} r^2 e^{-\beta_i r}\left[\sum_{v=0}^{n_{ri}} D_{vi} r^{v+2l_i}\right]^2$$

where

$$\alpha_{l_i m_i i} = 4\pi r^2{}_l a_{i m_i i}.$$

and substituting in equation (1),

$$F_n = \frac{D}{2\pi n}\sum_{i=1}^{N}\int_0^{D/2} \alpha_{l_i m_i i} r e^{-\beta_i r}\sum_{j=0}^{n_{ri}}\sum_{k=0}^{n_{ri}} D_{ji}D_{ki} r^{j+k+2l_i}\sin\frac{2\pi nr}{D}dr. \tag{6}$$

[3] A. Sommerfeld, "Wellenmechanisher Ergänzungsband," p. 72.

Let γ_i be the total quantum number of the ith electron. Then $\gamma_i=\gamma_{ri}+l_i+1$. The powers of r in the integrand run from 1 to $2(n_r+l_i)+1$, i.e. from 1 to γ_i-1 inclusive. Hence the integral is of the form:

$$I = \int_0^{D/2} \sum_{s=1}^{2\gamma-1} a_s r^s e^{-\beta_i r} \sin \frac{2\pi nr}{D} dr.$$

Each term of this integral can be integrated by parts successively, which reduces the power of r by 1 each step, and results in a series which, after substitution of limits, is of the form

$$\frac{\epsilon_1 n}{(\beta_i^2 + 4\pi^2 n^2/D^2)} + \frac{\epsilon_2 n}{(\beta_i^2 + 2\pi^2 n^2/D^2)^2} + \frac{\epsilon_3 n}{(\beta_i^2 + 4\pi^2 n^2/D^2)^3} + \cdots$$

Summing over the s's will change only the constants, ϵ.
Hence

$$I = \sum_{p=1}^{2\gamma_i} \frac{J_p n}{(\beta_i^2 + 4\pi^2 n^2/D^2)^p}$$

where the J's are constants and equation (6) becomes

$$F_n = \sum_{i=1}^{N} \sum_{p=1}^{2\gamma_i} A_{pi} / [B_i + (n/D)^2] \tag{7}$$

where the A's are constants and

$$B_i = 8\pi^2 m E_i / 4\pi^2 h^2.$$

In any practical case, $m=9\times10^{-28}$gm, $h=6.5\times10^{-27}$ erg sec, $E\leqq10^{-10}$ ergs for most of the electrons in atoms for which structure factors are determined. Hence

$$B \leqq 0.5 \times 10^{16} \text{ cm}^{-2} \leqq 0.5A^{-2},$$

and B will be less than $(n/D)^2$ for $(n/D)>0.7$ except, perhaps, the K electrons of heavy atoms and will usually be less than $(n/D)^2$ for $(n/D)>0.2$.

Expanding F_n in powers of $B/(n/D)^2$ we have,

$$F_n = a_1 / \left(\frac{n}{D}\right)^2 + a_2 / \left(\frac{n}{D}\right)^4 + \cdots \tag{8}$$

in which the a's are undetermined constants. Since

$$n\lambda = 2D \sin\theta$$

$$F_n = a_1/4\left(\frac{\sin\theta}{\lambda}\right)^2 + a_2/16\left(\frac{\sin\theta}{\lambda}\right)^4 + \cdots \tag{9}$$

$$= b_1 / \left(\frac{\sin\theta}{\lambda}\right)^2 + b_2 / \left(\frac{\sin\theta}{\lambda}\right)^4 + \cdots.$$

If it is desired to extrapolate an experimental structure factor curve

account must be taken of the effect of temperature. It has been shown[4] that the integrated intensity reflected at an angle θ is proportional to $e^{-B\sin^2\theta}$, where B is a function of the temperature and contains the factor $1/\lambda^2$.

Since $F_n^2 \backsim P_s$, the structure factor at any temperature, T, is

$$F_{nT} = F_{n0}e^{-(B/2)\sin^2\theta}$$

and Eq. (9) becomes:

$$F_{nT} = e^{-(B/2)\sin^2\theta}\left[b_1/\left(\frac{\sin\theta}{\lambda}\right)^2 + b_2/\left(\frac{\sin\theta}{\lambda}\right)^4 + \cdots\right]. \tag{10}$$

Waller[5] finds a function for B which for Na at 290°K gives $B = 3.74/\lambda^2$.

Using this value of B the first two terms in Eq. (10) were fitted by least squares to the structure factors computed by Holbrook[6] from Hartree's[7]

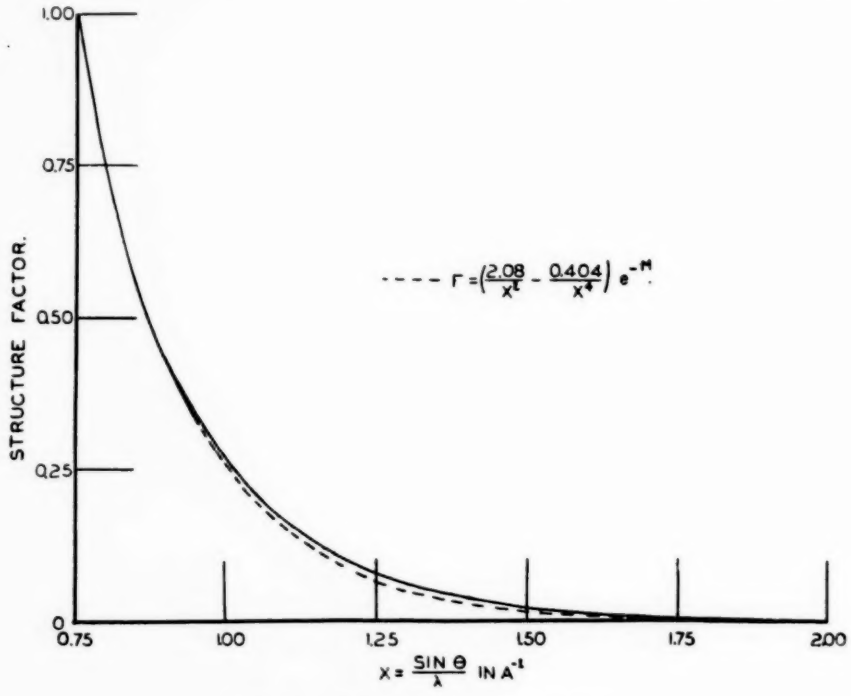

Fig 1. Extrapolated structure factors.

electron distribution for Na^+. The constants b_1 and b_2 were determined to fit the computed structure factors over the range from $(\sin\theta)/\lambda = 0.75$ to $(\sin\theta)/\lambda = 0.95$, which is about the end of the measurable values. Using these values of b_1 and b_2 the curve was extrapolated to $(\sin\theta)/\lambda = 2.00$. Fig. 1 shows the computed and extrapolated structure factors. The maximum deviation of the extrapolated curve from the true structure factor is 0.015

[4] P. Debye, Ann. d. Physik **43**, 49 (1914).
[5] I. Waller, Zeits. f. Physik **17**, 398 (1923).
[6] B. D. Holbrook, A paper not yet published.
[7] D. R. Hartree, Proc. Camb. Phil. Soc. **24**, 189 (1928).

electron and the fit is much better in most places. The entire structure factor for Na^+ is not shown since the vertical scale would need to be compressed ten fold to do so, and on such a scale the deviations of the extrapolation from the true values would not be noticeable.

Application to Scattering from Gases

It might be noted here that an exactly analogous treatment can be applied to the electron distribution as determined from gas scattering. In this case[8]

$$U = Zr \sum_{n=1}^{\infty} A_n \sin \frac{2\pi nr}{2a} \tag{11}$$

where Z is the atomic number, a the radius of the atom, and A_n is a function of the intensity of x-rays scattered at angle ϕ. n is given by $n = (4a/\lambda) \sin (\phi/2)$. In Eq. (11), the A_n replaces the nF_n and the $2a$ replaces D in Eq. (1). Hence Eq. (8) can be replaced by

$$A_n = (n/D)[a_1/(n/D)^2 + a_2/(n/D)^4 + \cdots] \tag{12}$$

$$= \frac{4}{a} \frac{a_1}{\left(\frac{\sin \phi/2}{\lambda}\right)} + \left(\frac{4}{a}\right)^3 \frac{a_2}{\left(\frac{\sin \phi/2}{\lambda}\right)^3} + \cdots$$

$$= b_1 / \left(\frac{\sin \phi/2}{\lambda}\right) + b_2 / \left(\frac{\sin \phi/2}{\lambda}\right)^3 + \cdots . \tag{13}$$

In conclusion the writer wishes to express his thanks to Professor A. H. Compton for suggesting this problem and indicating the general method of attack.

[8] A. H. Compton, Phys. Rev. 35, 933 (1930).

THE RANGE OF THE α PARTICLES FROM THORIUM

By G. H. Henderson and J. L. Nickerson
Dalhousie University, Halifax, N. S.

(Received September 5, 1930)

Abstract

The range of the α particles from thorium has been found from Wilson expansion chamber photographs to be 2.59 ± 0.05 cm. This agrees reasonably well with the Geiger-Nuttall relationship and greatly extends its applicability.

Introduction

THE ranges of the α-particles from most radioactive substances are known to a few tenths of one percent. The least accurately known is thorium, the longest lived of all the radioelements, for which only one determination worthy of consideration has been made. This was in 1911 by Geiger and Nuttall[1] and later corrected by Geiger[2] to the value 2.90 cm at 15°C and 760 mm. A more recent but tentative value of 2.75 cm was made by one of us[3] but the uncertainty involved was felt to be too great. This uncertainty in the range of thorium is the more regrettable since these values differ markedly from that predicted by the Geiger-Nuttall relationship between range and transformation constant. In view of recent theories of nuclear structure and α-particle emission it is of great interest to determine if this discrepancy is real or only due to experimental error.

Method

The difficulty in determining the range for thorium lies in its weak activity, which precludes the use of the usual methods. The method adopted was that of photographing the tracks in a Wilson expansion chamber, modified to deal with this inactive source. The thorium source was made as extended in size as possible, covering most of the wall of the chamber, while automatic photographing had to be dispensed with to economize film and the photographs taken by the operator after the appearance of the tracks. The practicability of this method had already been proved in this laboratory for the α-particles from UI and UII, by Laurence,[4] whose paper may be referred to for details.

The Wilson chamber was about 6 cm in diameter, actuated by a spring and cam mechanism and driven by a motor at the rate of 15 expansions per minute. On the appearance of an α-particle track an electrical contact made by the operator opened the camera shutter, shut off the motor and applied

[1] Geiger and Nuttall, Phil. Mag. **22,** 613 (1911).
[2] Geiger, Zeits. f. Physik **8,** 45 (1922).
[3] Nickerson, Trans. N. S. Inst. Sci. **17,** 172 (1929).
[4] Laurence, Phil. Mag. **5,** 1027 (1928).

a brake. Readings of temperature and pressure were then made. The camera had an f. 4.5 lens and used moving picture film. Light was supplied by a carbon arc.

Besides the tracks from thorium there were also longer tracks from isotopes which might strike the top or bottom of the chamber. It was necessary to photograph a large number of tracks so as to smooth out the probability variations in this background before the range of the α-particles from thorium itself could be clearly distinguished. The work was very tedious, for on the average about 200 expansions were necessary per track. Photographs of about 900 tracks were obtained, of which some 420 were judged sharp enough to be measured satisfactorily.

Source

Two samples of thorium were used. One was a commercial sample of thorium nitrate, which contained a small amount of the isotope ionium, arising from the small percentage of uranium ordinarily mixed with thorium ores.

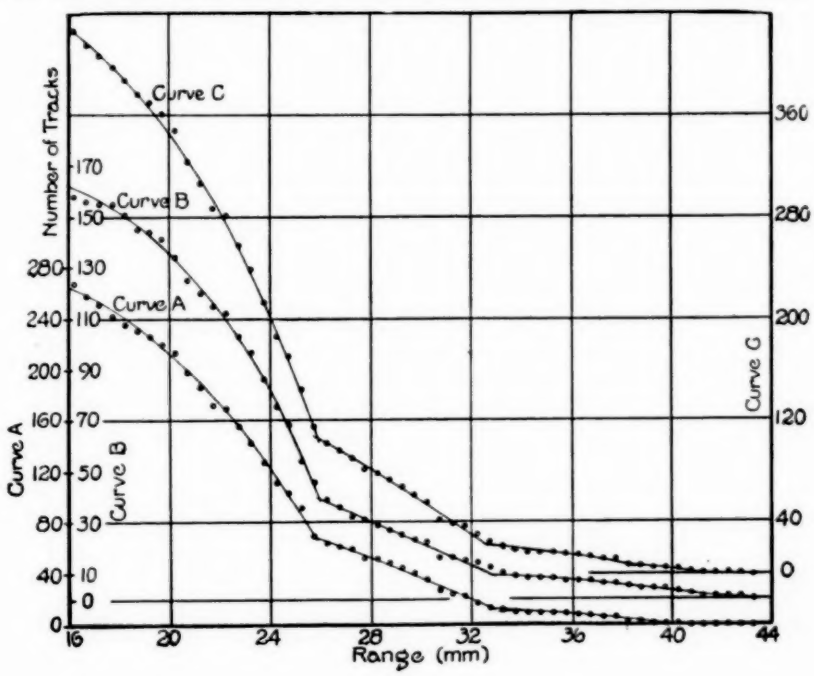

Fig. 1.

The other was a small sample of thorium hydroxide practically free of uranium, kindly furnished by Professor Soddy.

After much experimenting, the following method of preparing the sources was adopted. The sample was put into solution, some lead nitrate added and then the lead together with radioactive isotopes was precipitated by hydrogen sulphide. The thorium remained in solution and was then precipitated as hydroxide by ammonia, leaving ThX in solution. The hydroxide was dried, turned into the oxide by heating and then ground very fine in an agate mor-

tar. The thorium oxide dust was then brushed on to mica strips, which had been covered on one side by very soft wax. The finest of the dust adhered to the wax and with some practice it was found possible to obtain sources of the desired thickness, which appeared very uniform under low magnification. The thickness was determined by weighing and was generally made equivalent to about 1 mm of air. The mica strips were about 11×0.6 cm and covered most of the wall of the chamber, leaving a space to admit the light. To minimize the growth of later products, a source was not used for more than 30 hours after preparation but was replaced by a freshly made one.

Results

The tracks were measured, corrected for pressure, temperature, water vapor, finite thickness of source and obliquity of tracks as described by Laurence.[4]

The results obtained are shown in Fig. 1. The abscissae represent the range in air at 15°C and 760 mm and the ordinates the number of tracks greater than the corresponding range. Curve *A* represents the results with uranium-free thorium, curve *B* those with commercial thorium, and curve *C* the combined results. The axis of abscissae of each succeeding curve has been raised for clearness.

It is satisfactory to find that the two different samples of thorium give clear-cut and almost identical ranges. From the combined results the range of thorium α-particles is taken to be

2.59 ± 0.05 cm at 15°C and 760 mm pressure.

The Geiger-Nuttall Relationship

This relationship is best illustrated by a diagram. In Fig. 2 $20+\log\lambda$ (where λ is the transformation constant) is plotted against the log of the range at 15°C. Most of the values for the ranges are due to Geiger, the value of UI being that of Laurence[4] and that for Th our present value. The error in each range, as assigned by the experimenters themselves, is indicated by the size of the dot or circle representing the α-particle concerned.

This diagram shows that both UI and Th fit the straight lines reasonably well. Even if UI and Th be left out it can be seen that no straight line can be drawn for any of the three radioactive families which will fit the results within the limits of experimental error. In fact a straight line can be drawn as shown passing through all points of the thorium family including thorium with an average deviation no greater than that shown by least squares[5] for the five remaining members of that family. (In considering these deviations, of the order of less than 1 percent, it should be remembered that the range itself is defined in a somewhat arbitrary manner.)

Thus the conclusion may be drawn that Th and UI fit the Geiger-Nuttall relationship about as well as the other substances. It should be pointed out that this represents an enormous extension of the applicability of this relationship. In the case of thorium it involves a change of the transformation

[5] Meyer u. Schweidler, Radioaktivität, 2nd ed. p. 50.

constant by a factor of 10^{10}, a change greater than the whole range of values covered by the remainder of the family.

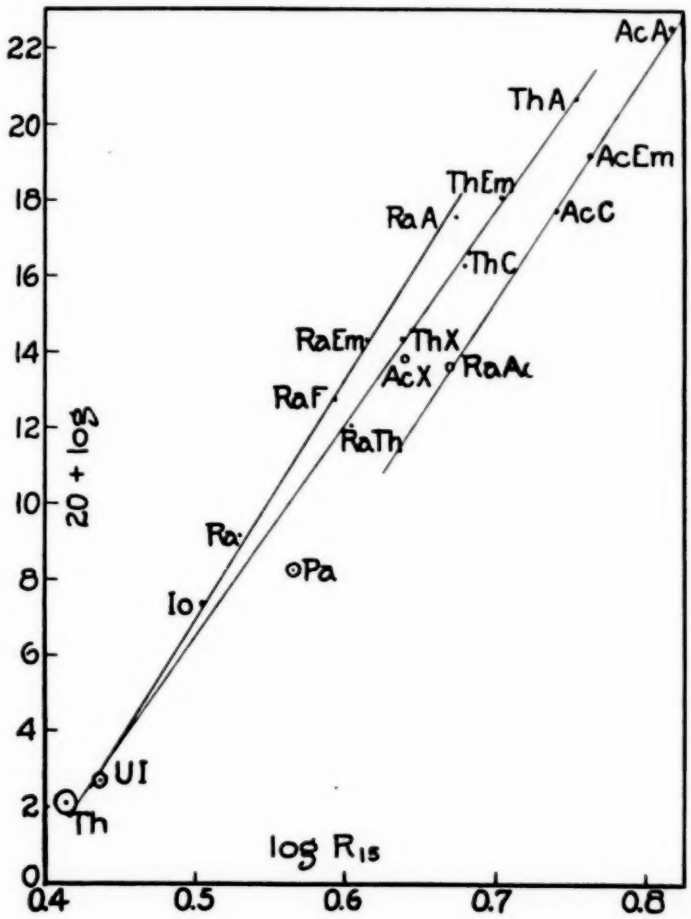

Fig. 2.

REMARKS

It will be noted that the number of thorium tracks does not become constant with decreasing range, owing to the geometrical conditions imposed by the boundaries of the chamber.

Traces of the ranges of other α-particles from isotopes are to be seen on the curves. That of ionium is fairly clear at about 3.26 cm (accepted range 3.194 cm) Further along are slight signs at 3.8 cm (protoactinium, 3.67 cm?) and at 4.1 cm (radiothorium 4.02 cm?). Tracks longer than about 4.3 cm could not be measured in the chamber and tracks as long as those of radiothorium would be very rare owing to the small permissable solid angle. The kink in the curve at about 3.0 cm would seem to be due to probability effects.

In conclusion we wish to thank Professor F. Soddy of Oxford for purifying and furnishing the sample of thorium.

POSSIBILITIES OF THE OSCILLATING ARC IN SPECTROCHEMICAL ANALYSIS

By E. Z. Stowell and W. S. Huxford
University of Michigan, Ann Arbor

(Received September 3, 1930)

Abstract

It is shown experimentally that none of the alkali metals will allow radio-frequency oscillations to be generated across an arc in hydrogen, but that the alkaline earths will do so: a confirmation and extension of previous work. Spectra have been photographed of the two groups of elements when burned in the hydrogen arc, and the intensification and reduction of the lines of various elements is described. The effect of a minute quantity of Mg in large amounts of Rb and Na is described in detail, as well as the method by a quantitative estimate of the amount might be reached. No satisfactory explanation for the complicated phenomena of the oscillating arc has yet been found.

I. Introduction

A PREVIOUS paper[1] established as a fact of experience that an atmosphere of hydrogen is essential for the production of undamped high-frequency oscillations across an arc, and that in general these oscillations are then generated only if the cathode contains an element of even atomic number in its composition. Upon examining the spectra of these even elements while the arc is in the oscillating state, it is found that the even elements are intensified out of proportion to the odd. This suggests the use of an arc of this character in spectrochemical analysis.

The following work was done with a home-made arc, designed to permit rapid changes of electrodes. The arc operated on 220 volts dc, drawing 5 amps. on striking and 2.25 to 2.5 amp. while oscillating. Both electrodes were watercooled; the water did not reach the electrode tips, which could therefore be unscrewed from the arc without danger of water leakage. For the elements studied in these experiments it was necessary to use hollow copper cups as cathodes, in which was placed the element to be studied. The blank cups by themselves would not sustain a dc arc in hydrogen; this copper contained Ti and a small trace of Ca as impurities. Practically all spectra described below show these elements so that the effects cannot be ascribed to them. Commercial hydrogen was fed from a tank into the arc chamber and burned at the exhaust. The gas pressure inside the chamber was therefore fixed at one atmosphere. The arc flame was along the axis of the magnetic field. A radio-frequency circuit tuned to about 1000 meters wave-length was connected across the arc.

The spectrograph used was a double prism combination of glass built in the physics shops. The region photographed was 3500–5200A, with Eastman

[1] Stowell and Redeker, Phys. Rev. **34**, 978 (1929).

Process plates. Exposures intended for comparison with one another, as, for example, an arc in the oscillating state as against the same arc in the non-oscillating state, were taken on the same plate and given identical exposures with the same arc current.

II. Study of the Alkalis and Alkaline Earths as Cathodes in the Oscillating Arc

The work cited in the previous paper[1] had indicated that the alkalis would not permit the generation of radio-frequency oscillations, while the alkaline earths would allow the oscillations to be generated. This has now been tested for the alkalis Li, Na, K, Rb and Cs, and for the group II elements Be, Mg, Ca, Sr and Ba; and is found to hold for these 10 elements.

This suggests the possibility of using the presence of current in the oscillating circuit as an indication of the presence of the elements of group II; this possibility is discussed in Section V.

III. Spectra of Alkali Metals in Hydrogen

Although none of the alkali metals allowed oscillations to be generated, the spectrum of the dc arc in hydrogen was photographed for comparison with the alkaline earths. The nature of the spectra are indicated in Table I.

Table I. *Nature of spectra obtained with dc arc in hydrogen.*

Element	Observed	Balmer lines
Li	Li I, Na I, K I, RbI, Cs (trace) Cu, Ti	No
Na	NaI, K I, RbI, Ca I, Ca II, Sr I, Sr II, Ba I, Ba II, Cu, Ti	No
K	K I, Rb I, Cs I (trace) continuous spectrum, no Cu or Ti.	No
Rb	Rb I, Na I, K I, Cs I, Ca I, Ca II, Sr I, Sr II, Mg I. Cu, Ti.	Yes
Cs	Cs I, Rb I, continuous spectrum, no Cu or Ti.	No

The elements used were of the ordinary grade obtainable in a chemical laboratory and no effort was made to purify them further as the effect of the impurities was of interest.

Only one of the spectra showed Balmer lines; that using a Rb cathode. This spectrum is also noteworthy in that it is the only one showing Mg as impurity. Ca, Sr and Ba had appeared above with the Na cathode in the Table, but the presence of these three elements appears to be insufficient to excite the Balmer lines; the appearance of the Balmer lines must therefore be connected with the presence of Mg. Owing to the fact that one of the Balmer lines, H_β let us say, may be of the order of 100 times the intensity of the sensitive Mg triplet at $\lambda 3838$, it is possible that the presence or absence of H_β might prove a method of detection of traces of Mg so minute that the sensitive lines of the element do not appear. If, for example, the intensities on the Rb plate were all reduced by a factor of 10, H_β would still be easily observable while $\lambda 3838$ would be wiped out.

The only other interesting feature of these plates is the large amount of continuous spectrum using K and Cs, and the simultaneous disappearance of Cu and Ti lines.

IV. Spectra of Be, Mg, Ca, Sr and Ba in Hydrogen

As all these elements allowed oscillations to be generated, a comparison was possible between their spectra in air, and in hydrogen with both the oscillating and the non-oscillating condition. The latter condition was obtained by opening the oscillating circuit.

The comparison is shown in Table II. One effect readily seen is the tendency of the arc in hydrogen, particularly when oscillating, to bring out impurities that were weak or absent in the arc in air. The Be used, for example, did not show Mo and V impurity until burned in hydrogen. It happens that in this case the addition of the oscillating circuit did not bring out any new impurities. With the Mg cathode, the oscillating condition shows spectra of many more elements than in the non-oscillating condition, and even shows one element, Pb, which did not appear in the arc in air. With a Ca cathode, Mn is thus brought out, and with a Sr cathode, Mg.

Table II. *Comparison between arc spectra in air and in hydrogen (oscillating and non-oscillating) for the alkaline earth metals.*

Cathode Element	Arc in Air	Non-oscillating Arc in Hydrogen	Oscillating Arc in Hydrogen			
			Elements intensified	Elements weakened	Elements not in non-osc. arc	New Elements
Be	CaI, CaII, SrI, BaII MnI	CaI, CaII, SrII, BaI BaII, MnI, Mo, V, Fe, Balmer Lines, and 2 bands of BeH_2?()	CaI CaII MnI	Ba, Sr, Fe, Mo, V, Balmer lines		
	Cu, TiI, Be	Cu, TiI, TiII, Be	TiII	Cu, TiI		
Mg	CaI, CaII, SrI, SrII BaII, MnI	BaI, MgI, MgII and Balmer Lines	BaI MgI MgII	Balmer Lines	CaI CaII SrI SrII BaII MnI TiII	PbII
	Cu, TiI, MgI, MgII	Cu, TiI				
Ca	SrI, SrII, BaI, BaII	SrI, SrII, BaI, BaII, MgI, AlI and Balmer lines	SrI, SrII BaI, BaII MgI, AlI and Balmer Lines			MnI
	Cu, TiI, CaI, CaII	CaI, CaII, Cu, TiI, TiII	Ca			
Sr	CaI, CaII, BaI, BaII MnI (trace)	CaI, BaI, BaII, MgII and Balmer Lines.	CaI, BaI, BaII, MgII and Balmer lines		MnI CaII	MgI
	Cu, TiI, SrI, SrII	Cu, TiI, SrI, SrII	Cu, TiI, Sr		TiII	
Ba	CaI, CaII, SrI, SrII MnI (trace)	Balmer Lines	Balmer Lines		CaI, CaII SrI, SrII	
	Cu, BaI, BaII	Cu, BaI, BaII	BaII	Cu	MnI	

All of these spectra contain Balmer lines under all conditions. The addition of the oscillating circuit weakens the Balmer lines from Be and Mg and strengthens those from Ca, Sr and Ba.

V. Attempted Use of the Oscillating Arc in Quantitative Analysis

Six samples of Na_2SO_4 (with Ca impurity) were prepared with the following amounts of $MgSO_4$ as a known impurity: No. 1, 0%; No. 2, 0.0001%; No. 3, 0.001%; No. 4, 0.01%; No. 5, 0.1%; No. 6, 1.0%. No oscillations

were obtained with No. 1; Nos. 2–6 inclusive gave oscillations, somewhat unsteady but easily readable on a radio-frequency ammeter with a 3 ampere maximum scale reading. It seems certain that the oscillations resulted from the presence of the Mg and not the Ca. The Mg triplet at λ3838 did not appear until No. 6 was reached, so that in this case the presence of oscillations furnished a more sensitive criterion for the presence of Mg than the appearance of the sensitive lines of Mg. It is probable that smaller amounts of Mg than 0.0001% could be detected by replacing the radio-frequency ammeter by a thermogalvanometer or thermojunction.

The magnitude of the radio-frequency current in the above cases took approximately the theoretical value when oscillations occurred; i.e., the needle varied from zero to $(1/2^{1/2})$ dc amps. Hence no estimate could be made of the relative amounts of Mg from the current readings.

VI. Discussion

It is of interest to compare these results with those of Crew.[2] In the case of a dc Mg arc in a hydrogen atmosphere he finds weakening of the copper and calcium impurity. In the non-oscillating condition, we find the Mg triplet at λ5183, the Mg II doublet at λ3538, and the doublet of Ca II at λ3933–3969, all completely suppressed; all reappeared with the closing of the oscillating circuit. The three green lines of copper were suppressed in both conditions, but the doublet at λ4023–4063 occurred weakly in both. The vanishing of the CaII doublet is quite unusual, as it is well known for its persistence. λ4481 of MgII was increased in intensity several fold by the addition of the oscillating circuit.

Other investigators of the excitation of the MgII spectrum in the presence of hydrogen[3] were unable to excite either λ4481 or λ3538–3535. This was in a low-voltage arc free from the effects of cumulative ionization which probably occurs in an arc at atmospheric pressure. Hence the mechanism of the excitation of this spectrum is not as simple as indicated by their equation

$$Mg+H_2^+ \rightarrow Mg^{+\prime}+H_2.$$

In all of the oscillating arcs, the Balmer series is obtained, indicating the presence of atomic hydrogen. So far it has not proven possible to write a general equation between the energy of the various states of the hydrogen atom and the cathode vapor, after the manner of Mohler[4] and Kaplan,[5] which would account for the lines observed, and at the same time explain the preference of the oscillations for even-numbered cathodes, and the absence of oscillations in all gases except hydrogen.

[2] Crew, Phil. Mag. **7,** 312 (1929).
[3] Duffendack, Henshaw and Goyer, Phys. Rev. **34,** 1132 (1929).
[4] Mohler, Phys. Rev. **29,** 419 (1927).
[5] Kaplan, Phys. Rev. **31,** 997 (1928).

ELECTRO-OPTICAL MODIFICATION OF LIGHT WAVES

By L. H. Stauffer
Department of Physics, University of California

(Received August 30, 1930)

Abstract

Broadening of the satellites of the Hg green line λ5461 was observed when the light passed between the plates of a Kerr cell on which was impressed a varying E.M.F. having a frequency of 2×10^7 sec^{-1}. The E.M.F. was obtained by superposing the output of a vacuum tube oscillator upon a steady potential of about 7000 volts. The maximum oscillator voltage was about 5000 volts. With this voltage the fine structure of the Hg green line became so diffuse that two satellites having a separation of 0.045A were scarcely resolved by the Lummer-plate. The broadening was observed to increase rapidly with the oscillator voltage. The observed effect is predicted by the classical electromagnetic theory and the quantum theories of dispersion of Kramers-Heisenburg, Schrödinger, and Dirac. The high frequency voltage effects a rapid variation of the refractive index of the nitrobenzene in the Kerr cell which in turn produces a corresponding variation in optical path, giving the source a virtual velocity, and thereby producing a Doppler effect. The magnitude of the observed broadening is in agreement with the predictions of theory.

Introduction

IT HAS been shown experimentally by E. Rupp[1] that monochromatic light suffers a slight change in wave-length when sent through an electro-optical shutter actuated by a high frequency oscillator. Rupp's shutter consisted of a Kerr condenser with nitrobenzene as a dielectric, placed between crossed Nicol prisms. When an E.M.F. is applied to the Kerr cell plates, the dielectric becomes doubly refracting and the second Nicol allows some of the light to pass through it. When an alternating E.M.F. is applied, the beam is interrupted with a frequency dependent on the frequency of the applied field. If the shutter opens and closes n times per second, theory predicts that the emergent beam should contain the original frequency and two "side frequencies" differing by $\pm n$ from the original frequency. These beat frequencies, of course, are due entirely to the rapid interruption of the beam and should be present even if the beam were interrupted by a mechanical shutter.

Shortly after Rupp's results were published, Wawilow[2] and others pointed out another phenomenon which must be considered when an electro-optical shutter is used. A variation in field strength produces a corresponding change in the refractive index of the liquid in the Kerr cell which, in turn, effects a change in optical path. This variation in optical path would give the source a virtual velocity and, in accordance with classical electromagnetic theory (Doppler's principle) a change in frequency would result.

[1] E. Rupp, Zeits. f. Physik **47**, 72 (1928).
[2] Wawilow, Zeits. f. Physik **48**, 600 (1929).

The experiment here reported was undertaken with the hope of testing the adequacy of the classical theory in explaining the above mentioned effect. Though to be sure, the quantum theories of dispersion of Kramers and Heisenburg[3] Schrödinger,[4] and Dirac[5] are in agreement with the classical theory in this regard, there remains a reasonable suspicion that quantum phenomena might enter to modify the expected results. Indeed, such a possibility is suggested by a curious anomaly reported by A. Bramley.[6] He photographed the arc spectrum of iron through a water Kerr cell on which was impressed the output of a high frequency oscillator. With relatively low voltages, he was able to detect shifts of certain lines toward the red end of the spectrum—shifts in magnitude very many fold greater than expected from theory.

General Theory

Assuming the results of the classical electromagnetic theory, it is not difficult to deduce the frequency modification undergone by a train of light waves when it traverses a medium subjected to an electric field of varying intensity.

W. A. Michelson[7] has generalized Doppler's principle to cover the case of a rapid variation of the refractive indices of the media traversed by a light ray. If ν is the observed frequency of the light then according to Michelson's formulation

$$\nu = \nu_0\left[1 \pm \frac{1}{c} \sum_i \frac{d}{dt}(\mu_i l_i)\right] \tag{1}$$

where ν_0 is the frequency of the radiation as it leaves the source, c is the velocity of light in vacuum, l_i the distance traversed in a medium having an index of refraction μ_i and t the time. For the case of a single medium of fixed extent (1) reduces to

$$\nu = \nu_0\left(1 \pm \frac{l}{c}\frac{d\mu}{dt}\right) = \nu_0 \pm \Delta\nu. \tag{2}$$

If a change in refractive index is effected by applying an electric field of strength E_1, P. Langevin[8] has shown theoretically that

$$\frac{\mu_p - \mu_0}{\mu_s - \mu_0} = -2 \tag{3}$$

where μ_0 is the refractive index of the medium for zero field strength and μ_p and μ_s the indices for light polarized with its electric vector parallel and perpendicular respectively to the direction of the field. This relation has been

[3] H. A. Kramers and W. Heisenberg, Zeits. f. Physik **31,** 681 (1925).
[4] E. Schrödinger, Ann. d. Physik **81,** 108 (1926).
[5] P. A. M. Dirac, Proc. Roy. Soc. **A114,** 710 (1927).
[6] A. Bramley, Jour. Franklin Inst. p. 315, March 1929.
[7] W. A Michelson, Astrophys. Jour. **13,** 192 (1901).
[8] P. Langevin, Le Radium **7,** 249 (1910).

experimentally verified by Pauthenier[9] in his measurement of absolute retardation in the Kerr effect. It is also well established that the relative retardation in phase of the components of the ray vibrating parallel and perpendicular to the field is given by

$$\phi = 2\pi BlE^2 \tag{4}$$

in which B is the Kerr constant and ϕ is the retardation in radians. The difference in the optical paths of the two components is

$$\frac{\phi\lambda}{2\pi} = (\mu_p - \mu_s)l = BlE^2\lambda \tag{5}$$

in which λ is the wave-length in vacuum. This gives the relation

$$BE^2\lambda = \mu_p - \mu_s. \tag{6}$$

Expressions for μ_p and μ_s may now be obtained by combining (3) and (6), the result of which is

$$\mu_p = \mu_0 + 2BE^2\lambda/3 \tag{7}$$

and

$$\mu_s = \mu_0 - BE^2\lambda/3. \tag{8}$$

The frequency change $\Delta\nu$ for light polarized with its electric vector parallel to the applied field may now be obtained by taking account of equations (2) and (7). This yields.

$$\Delta\nu = \frac{\nu_0 l}{c}\frac{d\mu_p}{dt} \tag{8a}$$

or

$$\Delta\nu = \frac{2B\lambda_0\nu_0}{3c} l\frac{dE^2}{dt} \tag{8b}$$

but since $\nu_0\lambda_0 = c$

$$\Delta\nu = \frac{4}{3}BlE\frac{dE}{dt} \tag{8c}$$

Apparatus and Procedure

The experimental arrangement (see Fig. 1) consists essentially of a Kerr cell, K, coupled to a vacuum tube oscillator, a mercury arc, M, as a light source, and a Lummer-Gehrcke plate, L, as a spectroscope. The mercury arc was water cooled to reduce Doppler broadening and was operated at the lowest current density which would maintain a steady arc. Light from the arc passes between the plates of the Kerr cell and is polarized with its electric vector parallel to the field by the Nicol prism, N_3. A constant deviation prism D serves as a monochromator to separate the green line λ5461. The interference pattern produced by the Lummer plate may be observed

[9] M. Pauthenier, Comptes rendus **170**, 803 (1920).

visually or photographed at E. The retardation can be measured at any time during the course of the experiment by observing the deflection of the galvanometer, G, which is actuated by current from the photoelectric cell P. A beam of light from the incandescent lamp, S, is sent through the cell in a direction crosswise to the plates and is polarized by the Nicol, N_1 in a plane making an angle of 45° with the vertical. When a difference of potential is applied to the plates the vertical component is retarded and the horizontal component advanced so that the light leaves the cell elliptically polarized and part of it can pass the second Nicol, N_2, which is crossed with respect to N_1. As will be shown later, the arrangement may be used to measure the field applied to the cell.

The design of the apparatus is governed largely by equation (8c) which gives the frequency change in terms of the Kerr constant of the liquid used in the cell, the length of the plates, the field strength and its time derivative.

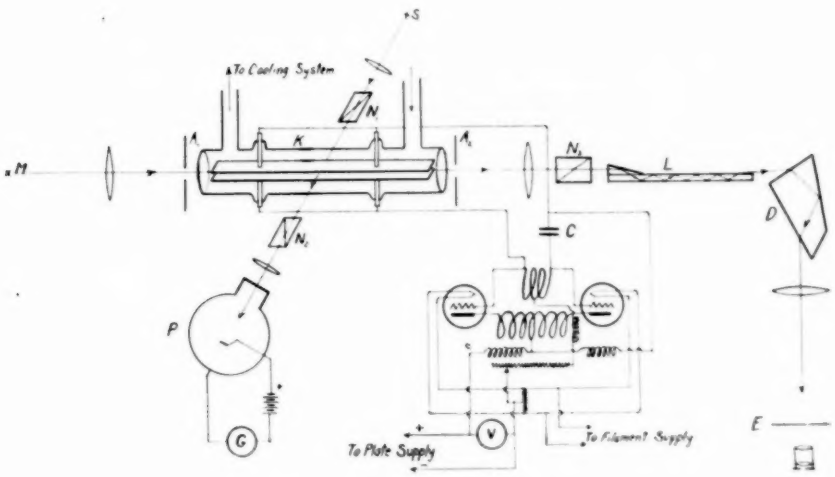

Fig. 1. Diagram of apparatus.

Nitrobenzene was chosen as the dielectric to be used in the cell for the reason that it has the largest Kerr constant of any known substance (3.5×10^{-5}). The quantity $E(dE/dt)$ may be made large by superimposing the oscillator output on a steady potential, in this case the plate potential of the oscillator.

The time rate of the field of course depends on the natural period of the oscillatory circuit, which is limited by the capacity of the Kerr cell. Since nitrobenzene has a specific inductive capacity in the neighborhood of 40, the capacity of even a small cell is comparatively high. The capacity was reduced as much as possible by making the plates narrow.

The Kerr cell used had nickel plates 10 cm by 2 mm with slightly rounded corners. The plate separation was 2 mm. Short tungsten leads of large diameter were used in order to reduce heating by the high frequency currents.

Considerable difficulty was at first encountered, due to the failure of the nitrobenzene to withstand the intense high frequency fields.

To reduce the conductivity to a minimum, the liquid was purified by treating with a weak base such as aluminum or calcium oxide to remove acids and then double distilling in vacuum during which process all water vapor was frozen out with liquid air. After such treatment, the liquid would

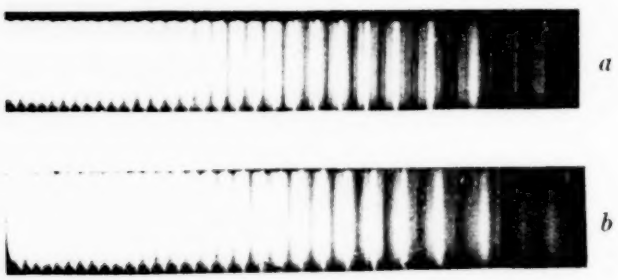

Fig. 2. Photographs of fine structure of Hg green line
(a) Unmodified spectrum. (b) Modified spectrum.

stand very high D. C. potentials, but heated badly, and broke down when subjected to high frequency fields. To keep the nitrobenzene cool, a water cooled circulatory system was devised, which consisted of a small four

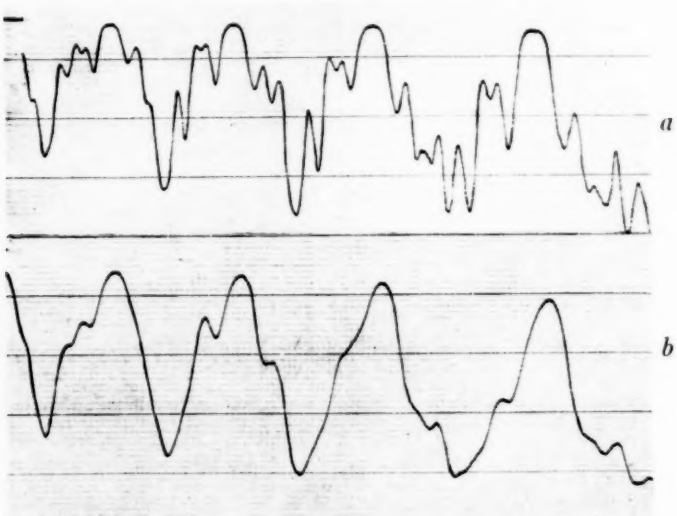

Fig. 3. Microphotometer curves. (a) Unmodified. (b) Modified.

bladed propeller rotating in a vertical chamber connected to the Kerr cell by tubes surrounded by water jackets. The whole was made of Pyrex glass to avoid contaminating the nitrobenzene. The liquid was found to withstand a much higher voltage when kept cool by this method.

A diagram of the push-pull oscillator used is shown in Fig. 1. Two 100 watt Radiotrons of the type UX-852 were employed with between 7000

and 8000 volts on the plates. The highest frequency that could be attained with the Kerr cell used was about 2×10^7 sec.$^{-1}$. The plate voltage of the oscillator is applied to the cell by inserting a large condenser C, and connecting the isolated terminal of the cell through a choke to the positive side of the plate circuit.

Visual observations of the fine structure of the mercury green line revealed a slight broadening of the components when the oscillator was operating. The effect was repeatedly confirmed by photographing. Fig. 2a and b shows the interference pattern of the Lummer-Gerhcke plate without and with the oscillator in operation. Fig. 3 shows microphotometer curves of the unmodified and modified patterns.

The procedure followed in photographing was to take an exposure under no voltage conditions with the circulator operating and then directly underneath on the same plate an exposure with the oscillator in operation. The overloaded oscillator could only be operated over intervals of about 10 seconds without danger of overheating the tubes and Kerr cell. The second exposure was, therefore, broken up into a number of 10 second intervals.

Discussion of Results

The appearance of the fine structure pattern of the Hg green line is shown in Fig. 2a. A large number of orders are present and as the photograph shows, the dispersion diminishes toward the lower orders. The main line and five satellites are clearly resolved on the original plates but the enlarged reproduction shows less detail. The designation and wave-length separations of the satellites are taken from a paper by McLennan[10] reporting some work on the Hg green line in which he used a Lummer plate. In

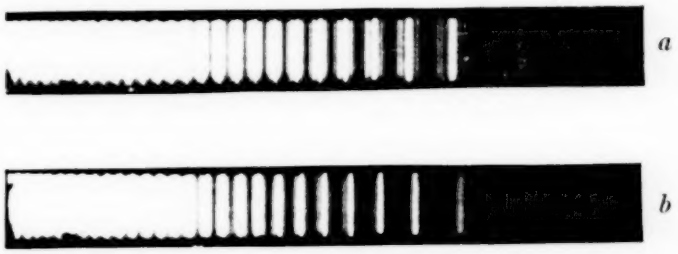

Fig. 4. Photographs of fine structure with reduced oscillator voltage.

all the photographs shown the negative satellites are on the right. The satellite -6 is separated from the main line by an interval of -0.237A and overlaps into the succeeding order where it is seen between the main line and the satellite $+3$. The wave-length separations from the main line of the satellites -6, -5, -4, $+3$ and $+4$ are -0.237, -0.102, -0.0698, $+0.852$ and $+0.128$ respectively.

The fine structure of the line as modified by a high frequency field of approximately 22,500 volts per centimeter superimposed on a steady field

[10] J. C. McLennan, Proc. Roy. Soc. **102,** 33 (1922).

of 36,000 volts per centimeter is shown by Fig. 2b. This gives a calculated broadening of over 0.01 Angstroms.

Microphotometer curves of the unmodified and modified lines are shown in Fig. 3a and b. The results obtained in a later trial with an oscillating field of 19,600 volts per centimeter and a steady field of 40,000 volts per centimeter are shown in Figs. 4 and 5.

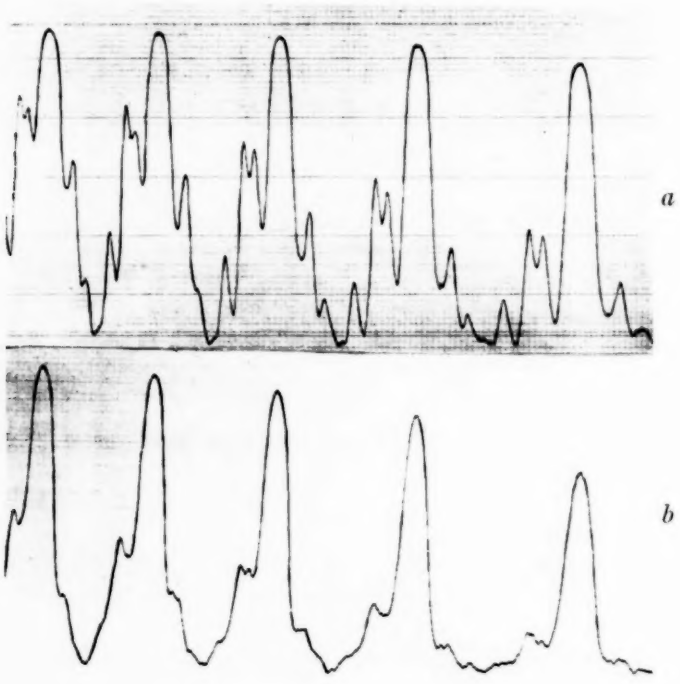

Fig. 5. Microphotometer curves. (a) Unmodified. (b) Modified.

In order to calculate the frequency change $\Delta\nu$ in terms of deflections of the galvanometer, G, and known constants of the apparatus it is necessary to modify equation (8b) by making the substitution

$$E = E_1 + E_0 \sin 2\pi nt$$

where E_1 is the steady field strength, E_0 the peak field strength of the oscillator, n the oscillator frequency and t the time. E_1 and E_0 are expressed in electrostatic volts per centimeter. Equation (8b) now becomes

$$\Delta\nu = \frac{2B\lambda_0\nu_0 l}{3c} \frac{d}{dt}(E_1 + E_0 \sin 2\pi nt)^2 \tag{9}$$

Taking the time average by integration over a quarter cycle gives

$$\frac{\overline{\Delta\nu}}{\nu_0} = \frac{8\lambda_0 Bnl}{3c}(E_0^2 + 2E_1E_0) \tag{10}$$

where $\overline{\Delta\nu}$ is the average value of the frequency change. Now if the intensity of the light reaching the photo-cell at any time t be represented by I we have in accordance with classical optics

$$I = I_0 \sin^2(\phi/2) \tag{11}$$

where I_0 is the intensity of light coming from the Nicol prism, N_1, and ϕ is the retardation. By substituting the value of ϕ given by equation (4) into (11) the expression for the intensity becomes

$$I = I_0 \sin^2 \pi B w(E_1 + E_0 \sin 2\pi nt)^2 \tag{12}$$

in which w is the width of the plates. In this experiment it can be shown that the average value of the retardation is small since w is only 2 millimeters. It is, therefore, permissible within the limits of error of the experiment to replace the sine by the angle itself. This is done to facilitate the integration of equation (12) to get the time average of the intensity I. The result of the integration is

$$\overline{I} = I_0\pi^2 B^2 w^2(E_1^4 + 3E_0^2E_1^2 + 3E_0^4/8) \tag{13}$$

Eliminating B between (10) and (13) the following expression is obtained

$$\frac{\overline{\Delta\nu}}{\nu_0} = \frac{8\lambda_0 nlI^{1/2}(E_0^2 + 2E_0E_1)}{3\pi cwI_0^{1/2}(E_1^4 + 3E_1^2E_0^2 + 3E_0^4/8)^{1/2}}. \tag{14}$$

Since the galvanometer deflections are small and the photoelectric current is proportional to the intensity, the ratio of intensities may be replaced by the ratio of the corresponding deflections. It is also more convenient to deal with the ratio of E_0 to E_1 than to use the equation (14) as it stands. Designating the ratio E_0/E_1 by a, equation (14) becomes

$$\frac{\overline{\Delta\nu}}{\nu_0} = \frac{8\lambda_0 nlD^{1/2}a(a + 2)}{3\pi cwD_0^{1/2}(1 + 3a^2 + 3a^4/8)^{1/2}} \tag{15}$$

or in terms of λ_0 the average change in wave length $\overline{\Delta\lambda}$ is

$$\overline{\Delta\lambda} = \frac{8\lambda_0^2 nlD^{1/2}a(a + 2)}{3\pi cwD_0^{1/2}(1 + 3a^2 + 3a^4/8)^{1/2}}. \tag{15a}$$

D_0, the deflection corresponding to the intensity I_0, may be obtained by uncrossing the Nicols by an angle θ and observing the deflection D_θ. D_0 is then given by the relation $D_\theta = D_0 \sin^2 \theta$.

The ratio, a may be obtained as follows. Let I_1 be the intensity of light reaching the photo-cell when a field E_1 is applied to the Kerr cell. Equation (13) then becomes

$$I_1 = I_0\pi^2 B^2 w^2 E_1^4 \tag{16}$$

When the high frequency field is superimposed the intensity is given by equation (13). Dividing (16) by (13) and replacing the ratio of intensities by the ratio of the corresponding galvanometer deflections one gets

$$\frac{D_1}{D} = \frac{E_1^4}{E_1^4 + 3E_1^2E_0^2 + 3E_0^4/8} = \frac{1}{1 + 3a^2 + 3a^4/8}. \tag{17}$$

The value of a may now be obtained with sufficient accuracy by plotting a curve of D_1/D for values of a ranging from 0 to 2. Knowing E_1 from the reading of the voltmeter, V, the value of E_0 is available when a is known. The reason for not measuring E_0 by means of a voltmeter will be evident to those familiar with the difficulties in making accurate measurements of large currents or voltages at high frequencies.

The ratio of the length to the width of the plates was corrected for edge effect by taking measurements with the photo-cell and crossed Nicol arrangement, lengthwise as well as crosswise of the plates with the field on. As equation (13) shows the intensity is proportional to the square of the effective path traversed in the field, it was thus found that the value of $1/w$ must be reduced by 8.5 percent.

At first thought it might seem easy to measure the change in wave-length by taking measurements on the microphotometer curves of the fine-

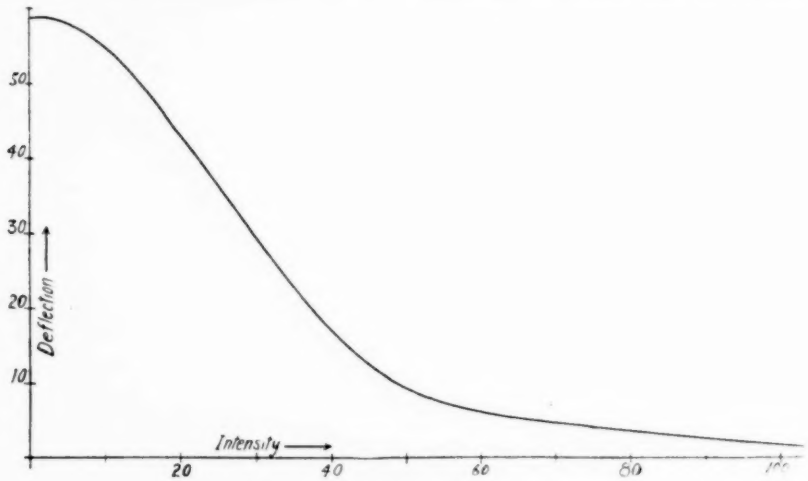

Fig. 6. Blackening curve for photographic plates.

structure patterns. The half-width of a satellite before the field was applied might be compared with the half-width of the modified satellite but this would probably not correspond to the average wave-length change given by equation (15a). It is also evident that the photographs of the modified and unmodified patterns are not comparable unless the exposures are the same since the width of the lines is influenced by the length of exposure. Since the ordinates of the microphotometer curves represent blackening and not intensity, it is necessary to know the blackening as a function of intensity for a given plate before two satellites can be compared. In view of these considerations one can only expect rough agreement between measured and calculated values of the wave-length change.

The procedure finally followed was to select a plate such as the one shown

in Fig. 4 where the modification is not so great as to obliterate the structure and to measure the change in half-width of the main line. To facilitate intensity measurements the unmodified fine structure was photographed, the Lummer plate removed and a slit and a Nicol prism placed in the path of the beam. A series of exposures was then taken on the same plate, the intensity of the beam being varied by rotating one of the Nicols a known amount before each exposure. The plate was then microphotometered and a curve of intensity against deflection was plotted. The curve is shown in Fig. 6. The deflections (plotted as ordinates) are measured from the line of absolute blackening on the microphotometer curves. Thus a large deflection means a low intensity. The intensity relations between the fine structure components were found to vary slightly from order to order of the interference pattern. It was found that over the range of the five highest orders in which intensity measurements were made that the intensity of the satellite +3 remained very nearly half that of the main line. In no order was the variation greater than six percent. The peak of the satellite +3 was therefore taken as the ordinate representing half-intensity for the main line in any given order. The dispersion was obtained by measuring the distance between the peaks of the satellites +3 and +4 which have a wave-length separation of 0.043A. The results obtained from the curves shown in figure 4 are presented in Table I.

TABLE I. *Results obtained from the curves of Fig. 4.*

Order	Dispersion mm/A	Broadening mm	Half-width Change/2 A
I	100	2.40	0.012
II	82.3	1.80	0.011
III	71.2	1.40	0.0098
IV	66.7	1.40	0.010
			0.0107 Mean

The average change in wave-length as given by equation (15a) is 0.0078A. The maximum change in wave-length may be secured by calculating the maximum value of dE^2/dt and introducing it in place of the average value as has been done. The calculation is straightforward but rather long. It yields a result which is 1.4 times as large as the average value, 0.0078. The factor 1.4 is not a constant but varies with a, the ratio of E_0 to E_1. The maximum value of $\Delta\lambda$ is therefore about 0.011 Angstroms, slightly greater than the mean value given in the table.

Thus, within the experimental uncertainty (about 20 percent), the magnitude of the observed change in frequency is in agreement with the predictions of the classical theory and the several quantum theories of dispersion. No anomalous effects of the kind reported by Bramley were detected in the course of the experiment.

The author is indebted to Professor E. O. Lawrence, who suggested this experiment, for his constant assistance and many helpful suggestions.

THE OPTICAL EXCITATION FUNCTION OF HELIUM

By Walter C. Michels
Norman Bridge Laboratory, California Institute, Pasadena

(Received September 6, 1930)

Abstract

With a discharge tube which has been considerably modified from the designs previously used, and with a technique specially developed to eliminate the effects of collisions of the second kind and ionization and recombination, the author has completed a study of the excitation function of helium for electrons with energies between the excitation potentials and one hundred volts. Two new features are introduced, namely, experimental conditions under which a linear dependence of intensity on either current or pressure is obtained, and an actual determination of the electron velocity distribution curve. The intensity curves, by themselves, agree fairly well with those obtained by earlier workers but, by the innovations mentioned above, it has been possible to correct these curves to obtain the true optical excitation function values. The corrected results show that each line has a maximum excitation probability either at or within a few tenths of a volt of the excitation potential, and that the probability drops off quite rapidly above this value, more rapidly for the triplet system than for the singlet.

Introduction

SINCE the publication of the original work of Hughes and Lowe[1] on the variation of the intensities of the lines of the helium spectrum with change of velocity of the exciting electrons, a large number of workers have made studies in this field. While the results of these investigations have been somewhat discordant, two papers, those of Hanle[2] and Elenbaas,[3] give results which show at least qualitative agreement between themselves and with the publication mentioned above. A study of the intensity-voltage curves given by these authors seems to enable certain conclusions to be drawn:

(1) All lines of the triplet system appear at their excitation potentials and show sharp maxima somewhere between these potentials and 35 volts.

(2) All lines of the singlet system increase in intensity rather rapidly just above the excitation potential, and show moderately flat excitation curves, with maxima between 60 and 150 volts.

While these points have been fairly definitely established in earlier investigations, the author has felt that certain discrepancies in the published results demanded further investigation. Elenbaas, for example, finds double maxima for most of the lines while Hanle, Hughes and Lowe find but one maximum for each line. The positions of the maxima also vary quite widely among the different investigations.

Before entering into a discussion of the present work, it may be well to

[1] Hughes and Lowe, Proc. Roy. Soc. **A104,** 480 (1923).
[2] Hanle, Zeits. f. Physik **56,** 94 (1929).
[3] Elenbaas, Zeits. f. Physik **59,** 289 (1930).

define just what interpretation shall be placed on the term "optical excitation function." In order that spurious results due to the apparatus may be eliminated, it would seem well to define this function as *the relative probability that light of a particular wave-length be emitted when an isolated atom experiences a collison (defined, for example, by kinetic theory considerations) with an electron moving with a specified velocity.* This definition imposes two definite restrictions on the experimental conditions:

(1) The requirement of isolation demands that the effects of collisions of the second kind, collisions with the walls, etc., be kept negligible, and that there shall be not more than a negligible amount of light emitted due to ionization and subsequent recombination.

(2) The exciting electron beam must be as nearly homogenous as possible, and the extent of departure from homogeneity must be determined.

The work now being reported was undertaken with these limitations definitely in mind and an attempt has been made to devise tests showing to what extent each requirement has been satisfied.

The Discharge Tube

The final design of discharge tube used for the excitation of the spectrum is shown in Fig. 1. Electrons from the ten mil tungsten filament were accelerated through the first slit, 2 by 20 mm, which was about 2 mm distant from

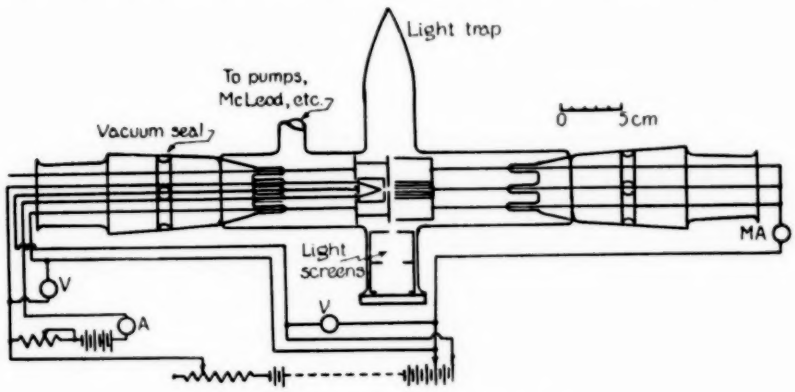

Fig. 1. Discharge tube with wiring diagram.

the filament. This slit was maintained at a potential difference of about sixteen volts above the second slit, about one mm away, and of the same size. Beyond this was a clear, field free space of 4 mm length, in which the emission was observed, and the plate, which was composed of a number of parallelopiped boxes, 20 mm deep. All electrodes were of nickel. The various potentials were maintained by a bank of storage cells.

A remark in regard to the choice of the filament may be desirable. In the early part of the work tubes with oxide coated platinum emitters, usually of the unipotential type, were tried, in the hope of obtaining a very homogenous electron beam. Velocity distribution curves taken on these tubes showed,

invariably, a very large percentage of slow electrons, distributed between zero velocity and that applied to the slits. This difficulty was finally traced to secondary electrons, emitted from the slits, due to barium distilled onto their surfaces from the cathode. With its low work function, this material acted as a particularly efficient secondary emitter. The loss in homogeneity due to the voltage drop across the tungsten filament was much more than compensated for by the decrease in these secondaries.

In addition to the change to a tungsten filament, certain other precautions against secondary electrons were taken. The difference of potential, previously mentioned, between the two slits served to sweep back any secondaries formed at the edges of the second slit. The particular plate design used was also adopted for the elimination of this effect. With the large metal surface and the small opening obtained by this construction, the plate acted as a black cavity, not only for the electrons but also for ultraviolet light from the excited atoms. Reflected, secondary, and photo-electrons were therefore neither recorded in the current measurements nor allowed to enter the space in which light emission was observed.

The tungsten filament introduced a further difficulty in the large amount of continuous light which it furnished. This light gave a background on the plates which was comparable with the exposures produced by the lines themselves until the light trap and screens shown were introduced. The tube was painted, outside, with a dead black lacquer, with the exception of the plate glass window through which observations were taken.

Frequent filament replacements necessitated the ground glass joint construction shown in the figure. Stop-cock grease was used only on the outer portions of the joints, and the vacuum seals were pumped continuously except during the actual exposures, to keep vapor from reaching the electrodes. The construction prevented baking, however, and the following method was used for cleaning the electrodes. After the apparatus had been opened to air, a charcoal trap, in close proximity to the tube, was baked at 350–400°C for about twelve hours. Liquid air was then placed on this trap and the filament emission gradually built up until about four milliamperes flowed to the plate, with an accelerating potential of 300 volts. Under these conditions the electrodes, near the filament, were glowing at a dull red. During the clean-up action, if the filament current was held constant, the current to the plate increased for a few hours, then decreased slightly to a constant value. In general, the heating and bombardment were continued for ten to twelve hours, with the vacuum pumps running. The tube was then ready for operation. For subsequent exposures, if air had not been admitted, bombardments of three to four hours were found to be sufficient. This clean-up technique was found to be absolutely essential, as will be explained later.

The current vs. retarding potential curve shown in Fig. 2a was obtained with this tube after such treatment and with the pumps maintaining a a vacuum of about 10^{-5} mm as measured by a McLeod gauge. The accelerating potential was 100 volts. The graphical differentiation of this curve gives the velocity distribution curve of Fig. 2b. By far the greater part of the elec-

tron beam is included within a five volt band, just accounted for by the filament potential drop. As the retarding potential was applied between the last slit and the plate, both of nickel, the 1.2 volt difference between the fastest electrons and the accelerating potential may be taken as the contact potential. This measurement checked, within the accuracy to which the voltage could be held constant during an exposure (about ± 0.3 volt), with the first appearance of the various lines at their excitation potentials. The "tailing off" of the distribution curve toward lower velocities may probably be attributed to a certain amount of electron reflection and secondary emission

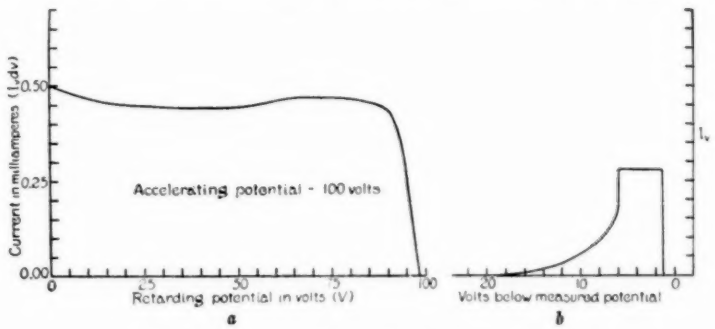

Fig. 2. Electron velocity distribution.

which was not eliminated. This region, however, accounts for only 30 percent of the total current, and this is much better than was obtained with any other type of tube construction which was tried.

The helium was purified as previously described[4] and was passed through the charcoal trap before entering the tube. This helium was never left in the tube for more than three or four hours of operation, after which it was pumped out and the clean-up process was repeated, before fresh gas was inserted.

Intensity Measurements

A photographic method was used for the measurement of the intensities, the optical set up being that shown in Fig. 3. A glass spectrograph, with an F 2.7 telescope lens was used for the photography. The extreme speed of this instrument made it possible to obtain exposures of satisfactory density with the discharge tube in 10 to 20 minutes, but made the obtaining of a continuous comparison spectrum a matter of some difficulty. In order to obtain a continuous spectrum of sufficiently low intensity, the scheme shown was resorted to. A ribbon filament tungsten lamp was mounted 70 cm from the optical axis. The light from a 3.25 mm section of the middle of the filament (which was 2 mm wide) was allowed to fall on the small right angled prism mounted on the axis. One face of this prism was ground to a focal length of 25 mm, so that a very much reduced image of the filament was formed on the optical axis. This image was used as a secondary source, and only the

[4] Hodges and Michels, Phys. Rev. **32,** 913 (1928).

light from it intercepted by the slit of the instrument was used for the calibration exposures. The Nicol prism, mounted directly in front of the slit, was arranged so that the two components of polarization could be measured separately and combined later to give the total intensity, thus eliminating errors due to the unequal treatment of the two components by the glass prism.

The 6 to 1 reduction obtained in the spectrograph made it impossible to use the "stepped reducer" method of plate calibration which had been utilized in previous work. It was necessary, therefore, to take a series of five or six calibration exposures. It seemed better, consequently, to eliminate the re-

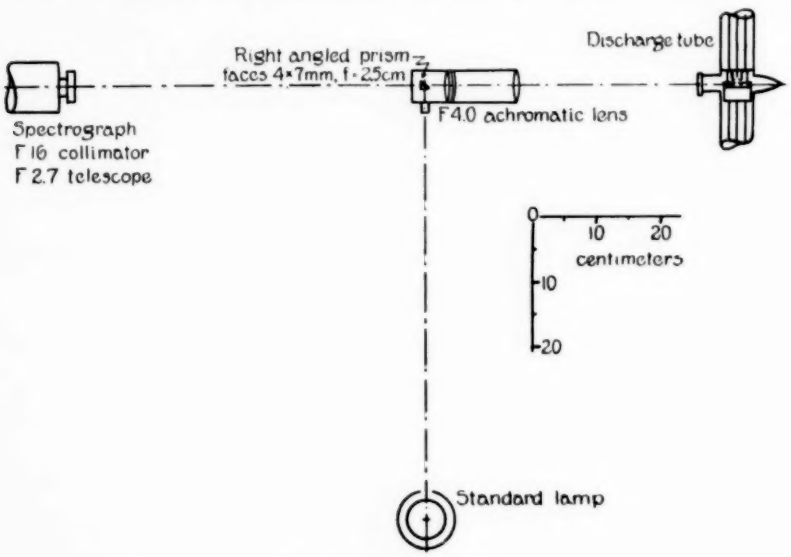

Fig. 3. Optical system.

ducers entirely, and to use a temperature variation of the standard lamp for the intensity steps. This was made particularly convenient by a new method of plotting the calibration curves.

In the older method, the density is plotted against the logarithm of the exposure, or, when the time is held constant, as it was in this work, against the logarithm of the intensity. This plot is widely used because it gives, over a large range of exposures, a straight line, in accordance with the Swartzchild formula. We now recall that tungsten, in the visible region, closely follows Wien's law:

$$I_{\lambda,T} = \epsilon c_1 \lambda^{-5} e^{-c_2/\lambda T}.$$

If, in this formula, we consider the emissivity, ϵ, to be a constant independent of temperature, as it is, very nearly, and vary the temperature, T, for a given wave-length, λ, we find that:

$$\log I_T = a - b/T,$$

where a and b are constants, so that, if the density be plotted against the reciprocal temperature, the straight line of the Swartzchild formula is re-

tained. A typical set of calibration curves for the Ilford panchromatic plates used in this investigation is given in Fig. 4. After the calibration curves had been obtained, the temperature of the tungsten lamp necessary to produce the same density as the helium exposure could be read from them, and the intensity corresponding to this temperature calculated from Wien's law. Correction was then made for the dispersion of the spectrograph to give the final intensities.

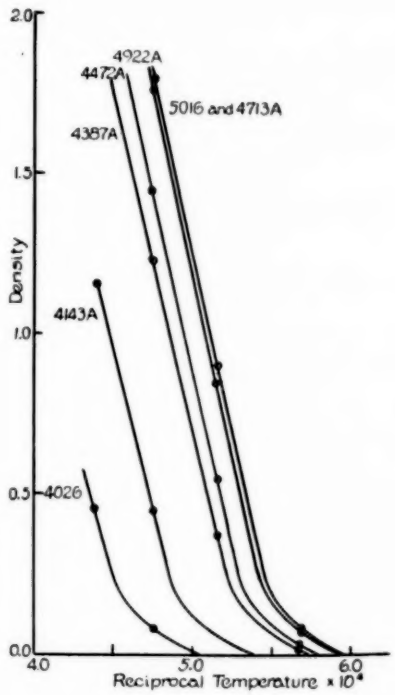

Fig. 4. Plate calibration curves.

The temperatures of the standard lamp were measured with a Leeds and Northrup optical pyrometer, the residual error of which was determined by a Bureau of Standards Calibration to be 2°C. The deviation measure of the temperature measurements was also about 2°C, so the temperature was accurate to about 3°C. Correction for the emissivity of tungsten was made according to the data of Forsythe and Worthing.[5]

It was possible to take fourteen exposures on a single plate. Of these, five, in general, were needed for continuous calibration exposures. The other nine were therefore used for helium spectra, taken under different excitation conditions. The plates were soaked in running water for five minutes, then developed according to the "brush method" recommended by Bloch.[6] With this treatment, it was found that errors introduced due to difference of posi-

[5] Forsythe and Worthing, Astrophys. J. **61,** 146 (1925).
[6] Bloch, Phot. J. **61,** 425 (1921).

tion on the plate were negligible. The plates were microphotometered in an instrument built at the Institute.

Intensity Variations with Current and Pressure

In nearly all previous investigations, tests of the dependence of intensity on the current and pressure have been tried. In most of these tests, a linear relationship has been expected but not found. If we define the excitation function for an isolated atom as was done above, it is obvious that the experimental conditions should be such that the intensity of any line should be proportional to the number of impacts between electrons and the atom in unit time. This number, moreover, is proportional to the current. Also, if the pressure is sufficiently low so that the mean free path is large compared with the linear dimensions of the apparatus, the kinetic theory exponential expression for the number of impacts can be expanded to the first order, and a linear relationship is obtained between the number of impacts and the pressure. From these considerations we should expect, if we have isolated behavior, a linear relationship between either intensity and current or intensity and pressure for any line.

If the condition of isolation is not satisfied, there are several possibilities. In the first place, two atoms, both excited to metastable levels, may collide. In this case, the number of metastable atoms should vary linearly with the current or pressure, so that a quadratic variation of intensity would be expected. Another possibility is emission due to ionization and recombination. For this phenomena we again have the density of ions and the density of electrons each depending linearly on the current and pressure, so we should once more expect a quadratic law. In the general case, then, when some atoms act as isolated, while others are influenced by surrounding atoms, the law of variation between intensity and current or pressure will be a combination of the linear and quadratic variations. In the first work done with the present apparatus, such a law was found to hold, with the quadratic term accounting for about half of the intensity at 100 volts, with a current density of 0.0125 amperes per sq. cm, and a pressure of 0.10 mm of mercury. As the voltage decreased, the importance of the quadratic term also decreased, becoming negligible at about 50 volts.

The difficulty with the above interpretation lies in the fact that the experimentally determined coefficient of the quadratic term is much larger than would be expected. Since the mean distance from any point in the space being observed to the electrodes was of the order of two millimeters, thermal agitation would carry any ion or atom to the wall in $5\ (10)^{-6}$ seconds. For ions, any positive space charge built up would greatly reduce this time. If the ions are neutralized and the metastable atoms drop back to the ground state, as would be expected on collision with the metal electrodes, the chance for the occurrence of these secondary phenomena would be very small, especially since, with the highest current and pressure ever used, collisions between an electron and any given atom occur once in two or three tenths of a second, and the concentration of metastable atoms, ions and electrons could not attain any very high value.

These difficulties of interpretation were removed by the clean-up treatment outlined above. It was found, after this treatment, not only that a linear relationship was obtained, but also that the constant of proportionality was identical with the coefficient of the linear term previously found. A typical plot of the results finally obtained is shown in Fig. 5, for the line 4472 A, taken at 100 volts. The spread of the observed points in this figure will also give an idea of the accuracy of measurement possible with the methods used. The variable chosen for the abscissa in this curve is the product of current and pressure. This, obviously, gives the same curve as either, plotted alone, would give, and at the same time saves space.

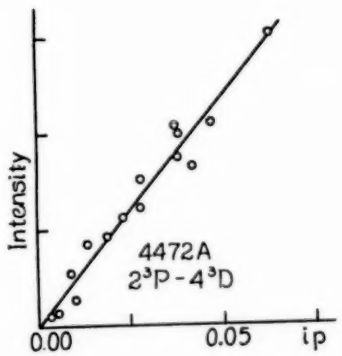

Fig. 5. Intensity variation with current and pressure.

The explanation, possibly, of the change in behavior after cleaning is that the electrodes, when coated with a layer of impurities (stop-cock grease or atmospheric molecules) act very inefficiently for the neutralization of the ions, and allow a large space charge to build up, thus increasing the relative importance of the recombination spectra. Data on the reflection of positive ions from dirty surfaces do not seem to be complete enough to give an answer on this point. Other evidence for the decrease of positive ions after the clean-up was given by the voltage-current curves, which showed no break in passing through the ionization potential.

The linear law finally obtained has been taken as proof that the atoms truly act in an isolated manner, and that contributions due to collisions of the second kind, recombination, etc., have been reduced to negligible proportions.

Intensity Variations with Voltage

Figs. 6 and 7 give the intensity-voltage relationships found. These curves were obtained by a series of exposures at pressures between 0.04 and 0.08 mm and with currents of 0.300 to 0.600 ma. By means of the linear relationships established, all these exposures could be reduced to a common pressure and current before plotting. While the relative intensities between the lines are approximately correct, those of wave-length shorter than 4500 A may be somewhat in error, due to absorption in the glass prism, through which the

line spectra and the continuous light did not have identical paths. This, of course, does not affect the shape of the curve for any individual line, but merely the relative heights.

In Fig. 6 the results for the singlet system are shown, plotted on a logarithmic scale for convenience. The weak lines of the singlet sharp series, while

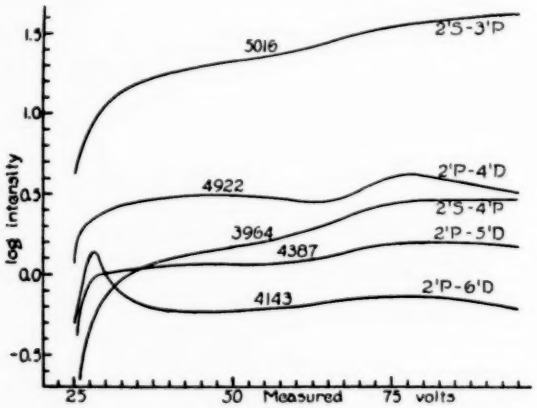

Fig. 6. Intensity-voltage relationships—singlet system.

they were resolved from nearby strong lines, were not far enough removed so that the microphotometer measurements could be relied upon, consequently no results are given for them. The first member of the diffuse series (6678 A) has also been omitted due to the continuous background from the tungsten filament, which was very appreciable in this region. It will be noticed that

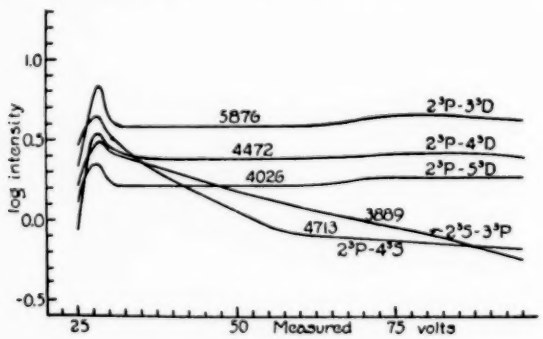

Fig. 7. Intensity-voltage relationships—triplet system.

the two lines observed in the principal series are apparently just approaching maxima at 90 to 100 volts, in quite good agreement with the results of Hanle and Elenbaas. In the diffuse series, 4922 shows two maxima, at 50 and 80 volts, as was found by Elenbaas. The other two lines observed show maxima at 80 volts, and 4143 has a sharp peak at 28 volts. This is the only singlet line showing this low voltage peak. A close examination of the curves will show that, in every case, a point of inflection occurs between 60 and 70 volts, indicating, apparently, some change in the excitation conditions in this region.

The behavior of the triplet system, as shown in Fig. 7, is somewhat different from that of the singlets. At least one member of each series has been observed in this case and all show sharp maxima at 28 volts. The behavior of the diffuse series is remarkably different from the other two, in that the intensity at voltages above the peak does not drop off rapidly. This series also shows maxima at about 80 volts as did the diffuse singlet series. All lines show the same inflection point between 60 and 70 volts as was shown by the singlets.

The Optical Excitation Function

In previous work, the plot of intensity vs. voltage given above has been taken as the curve of the optical excitation function, on the assumption of an absolutely monochromatic electron beam. With the experimentally determined distribution curve available, however, it is clear that, in the neighborhood of the excitation potential, part of the change in intensity, at least, is due to a change in the number of effective electrons, rather than to a variation in their velocity. The distribution curve shows that 96% of the electrons are included within a range of 10.8 volts. If the excitation potential of a given line, then, is 23 volts, it is clear that, taking into account the 1.2 volt contact potential, the effective current is increasing until a measured voltage of 35 volts has been reached. If the optical excitation function is defined for a monochromatic beam, which is not obtained experimentally, then the intensity will be given by:

$$I = C \int_0^\infty F(v)\, i(V_m, v) dv$$

where C is a constant, $F(v)$ is the optical excitation function for the voltage v, and $i(V_m, v)$ is the current distribution function (i.e. the height of the curve of Fig. 2b) for the same voltage, and for a given value of V_m as defined below. We know, however, that below the excitation potential V_0 the optical excitation function must have the value zero and that above a certain maximum voltage, V_m (1.2 volts below the measured potential), the current distribution function is zero. Making the corresponding change of limits and taking the constant into the function, we have:

$$I = \int_{V_0}^{V_m} F(v)\, i(V_m, v) dv.$$

Taking the derivative with respect to V_m.

$$\frac{dI}{dV_m} = F(V_m)\, i_m + \int_{V_0}^{V_m} F(v) \frac{di(V_m, v)}{dV_m} dv$$

where $F(V_m)$ is the value of the excitation function at the maximum voltage and i_m is the height of the flat portion of the distribution curve. Solving for $F(V_m)$ and choosing units so that i_m is unity:

$$F(V_m) = \frac{dI}{dV_m} - \int_{V_0}^{V_m} F(v)\frac{di(V_m, v)}{dV_m}dv.$$

Fortunately, when V_m is less than five volts above the excitation potential di/dV_m is zero throughout the range of integration, and the equation for $F(V_m)$ reduces to the first term. In this range, then, the optical excitation function may be directly determined from the slope of the intensity-voltage curve. This determination supplies a set of values of the function which may be combined with the values of di/dV_m read from Fig. 2a and graphically integrated to give the second term for the computation of the function at voltages not more than ten volts above the excitation potential. The new points thus obtained may be used in turn for calculating still higher voltages.

In Figs. 8 and 9 the results of these computations are shown. While the calculations could not be carried down to the excitation potential itself, due to the large error that would be introduced by a small error in the determina-

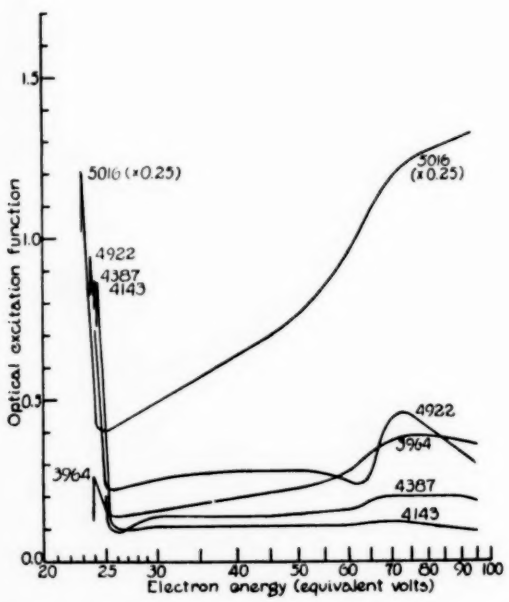

Fig. 8. Optical excitation function—singlet system.

tion of the velocity distribution, they have been carried to within half a volt of that potential. As the optical excitation function is still rising in value at that point, it has been assumed that the peak actually occurs at the excitation potential, and the curves have been extrapolated accordingly. In the figures, a logarithmic scale has been chosen for the voltages and parts of the curves approaching the peaks have been omitted in order to avoid congestion.

It will be noticed that the function, for all lines, exhibits a sharp peak at the excitation potential and a more or less constant value for all higher voltages. The width of the peak itself is, in general, about two volts. Whether

this width is real or is the result of experimental difficulties with voltage control, determination of velocity distribution, etc. cannot be decided with the present data.*

As would be expected from Figs. 6 and 7, the triplets are distinguished from the singlets by the fact that, in general, their ratio of peak height to background height is greater. The singlet principal series seem to be anoma-

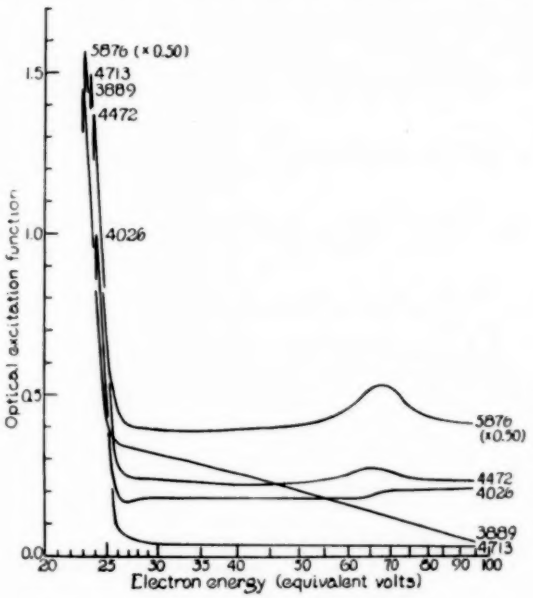

Fig. 9. Optical excitation function—triplet system.

lous in that its background value is of the same order of magnitude as the height of its maxima, and the two members observed show a much greater ratio of intensities than do the succeeding members of any other series. This may be connected with the fact that the normal state of the atom is a ^1S level, with allowed transitions to the ^1P levels.

Conclusions

We may summarize the new facts in regard to the optical excitation function of helium which have been brought forward in this investigation:

(1) It is possible, by proper apparatus and technique, to obtain experimental conditions under which the atoms act in an isolated manner, with no appreciable effect of recombination. The test for this condition is a linear dependence of intensity on either current or pressure, within a limited range.

(2) The optical excitation function has been shown to have a similar behavior for all lines, in that a sharp maxima is observed either at or very near to the excitation potential.

* It would seem probable that this peak may acutually consist of a series of maxima here unresolved, corresponding to the various excitation levels of the helium atom.

(3) Between 60 and 70 volts an irregularity occurs in the function, possibly due to some new mode of excitation entering in this region.

(4) The singlet and triplet systems are distinguished by the fact that, in the former, excitation is accomplished with fairly high probability by electrons with all energies above that just necessary for excitation, while, in the latter, those electrons with just sufficient energy to excite are much more efficient than those with greater energy.

In conclusion the author wishes to express his extreme gratitude to Drs. R. A. Millikan, I. S. Bowen, and W. V. Houston, whose constant interest has been of great aid in the completion of this investigation. He also wishes to thank Mr. A. B. Anderson for assistance in taking some of the data.

ORGANIC REACTIONS IN GASEOUS ELECTRICAL DISCHARGE I. NORMAL PARAFFIN HYDROCARBONS

By Ernest G. Linder*
Cornell University

(Received September 4, 1930)

Abstract

An apparatus is described for subjecting vapors to an electrical discharge. Vapor pressure and current are variable. Different fractions of the gaseous reaction products can be collected and their rates of accumulation measured. A study of n-decane vapor with this apparatus, with current values of from 0.5 to 2.5 m.a., voltage approximately 450 volts, and pressures from 0.2 to 4.5 mm of mercury, indicates that electric conduction in gases may follow an electrochemical equivalence law similar to Faraday's law of electrolytic conduction in liquids. Evidence has been obtained showing the amount of reaction to be proportional to the current, and independent of voltage and vapor pressure. Among the reaction products is a wax-like substance which deposits on the cathode only. The rate of production of gaseous reaction products has been measured for various values of discharge currents and vapor pressure. Curves and tables are given showing the relation between molecular size and rate of production of various fractions of the gaseous reaction products, for a series of seven normal paraffin hydrocarbons. A brief theoretical discussion is given.

Introduction

OF THE many investigations of electrical discharges in gases the greater part has been carried out with stable gases, whereas gases which undergo chemical changes in the discharge have been comparatively neglected. The work described below is the first set of a series of measurements which may eventually include all available hydrocarbons, and possibly also some oxygen-containing compounds, such as alcohols, ethers, ketones and esters. The purpose of the investigation is to try to shed some light on chemical action in electrical discharge, and to contribute something to the knowledge of the relation between molecular structure and chemical reactions, especially in regard to hydrocarbon chain structure.

Apparatus and Procedure

The apparatus (Fig. 1) consists of a bulb E for containing the liquid hydrocarbon, the discharge chamber D, the trap T, the mercury vapor pump P, and the storage chamber S, from which tubes G and F lead to a McLeod gauge and oil pump respectively. The bulb E can be immersed in a constant-temperature bath and runs made at constant vapor pressure. The discharge chamber D consists of a two-liter Pyrex bulb; the purpose of the large volume being to minimize any possible influence of the walls on the chemical

* Detroit Edison Research Associate. The work described in this article is a part of an investigation of the fundamentals of organic dielectrics being carried on at Cornell University. It is supported by a fund provided by the Detroit Edison Company.

action. The two aluminum disk electrodes are about 2.5 cm in diameter and about 8.5 cm apart. They are mounted on heavy, glass-covered tungsten wires which in turn are sealed through ground glass stoppers, so that the electrodes may be removed from the bulb for cleaning. The trap T is of the ordinary type except that there is a ground joint near the top to facilitate cleaning, and the inside tube is cut shorter than usual and is flared at the end to prevent clogging by frozen hydrocarbons. The storage chamber S has a capacity of about 13 liters. The electrical energy for the discharge is supplied by a transformer in series with a single kenotron.

When the apparatus is in operation a continuous current of vapor flows from E to T where it condenses. The chamber D is therefore filled with hydrocarbon vapor whose pressure is determined by the temperature of E. In the few cases where runs were made at temperatures higher than that of

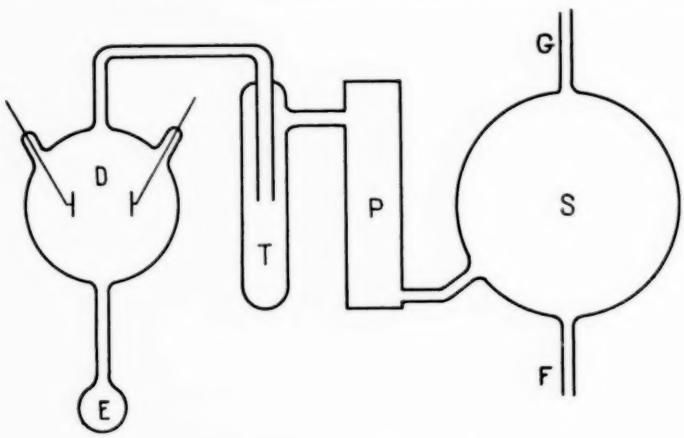

Fig. 1. Diagram of apparatus.

the room, E was removed, the hydrocarbon was placed in D itself, and D was entirely immersed in a constant-temperature bath. The runs were all made with such a high rate of vapor flow from E to T that all gaseous reaction products were swept out of D before there was any appreciable reverse reaction. This was shown by the fact that the results were independent of the vapor pressure, and consequently of the rate of flow. The discharge may therefore be considered as taking place through essentially pure hydrocarbon vapor.

Either liquid air, or a slush of carbon dioxide snow and ether was used as a refrigerant for the trap T, depending upon what fraction of the gaseous products it was desired to collect. With carbon dioxide cooling, n-hexane vapor was found to pass easily through the trap, while n-heptane was stopped. Since the vapor pressures of these two substances at $-77°C$ are about 0.1 and 0.02 mm of mercury respectively, it can be concluded that substances of vapor pressures below 0.02 mm at the temperature of the trap will not pass, whereas those of vapor pressures above 0.10 mm will pass. This means, for example, that in the normal paraffin series, with liquid air cooling, only

H_2, CH_4 will pass, while with carbon dioxide cooling H_2, CH_4, C_2H_6, $\cdots$, C_6H_{14} will pass, and higher members of the series will be stopped.

Runs were made on seven normal paraffin hydrocarbons, n-pentane, n-hexane, n-heptane, n-octane, n-decane, dodecane, and n-tetradecane. All were obtained from the Eastman Kodak Company, and were of the highest degree of purity provided by them, except n-pentane which was the "practical grade." However it is believed that small amounts of impurities have no appreciable effect on the phenomena reported here, since in a series of about fifty runs, made on the same sample of n-decane, the results toward the end of the series were the same as at the beginning. A similar observation was made also with some of the other hydrocarbons, but the number of runs was not so great.

Results

The discharge was run with currents from 0.5 to 2.5 m.a. for the n-decane measurements, and 1.0 m.a. for the other substances. The voltage could not be varied independently; it made wide fluctuations (sometimes as large as 25 percent) about 500 volts for all compounds. In appearance the discharge was essentially the same for all hydrocarbons investigated. There was only a very slight visible glow around the cathode, and frequently none at all. The glow was most apparent at the lower pressures, and hardly perceptible at all at pressures as great as 1.0 mm. The most conspicuous feature was the large number of sparks scintillating on the surface of the cathode. The sparks were small and bluish, and appeared in about equal numbers on the back and front of the disk. At the beginning of a run, when only a thin layer of wax had formed, they appeared evenly distributed, but later on, became more or less concentrated in small regions or spots. These spots finally became black as if the wax had been carbonized. Sparks also appeared on the surface of the anode, but they were much fewer in number and did not shift about, remaining fixed and glowing for minutes at a time. They were yellow or white rather than blue in color.

Previous work has shown that in general the effect of an electrical discharge in a hydrocarbon gas is to cause an apparently complicated chemical reaction resulting in solid, liquid and gaseous products. With the writer's apparatus the solid products were deposited mostly upon the cathode with slight traces of deposits on the glass walls, the gaseous products were pumped over into the storage chamber *S*, while the liquid products (if any) condensed in the trap. However, no evidence of liquid products was found, the same sample of n-decane having been run through the apparatus about fifty times without showing evidence of contamination or change of any sort.

The wax which formed on the cathode has not been analyzed by the writer, but analyses of similar, if not identical compounds by others[1] indicate

[1] S. C. Lind, *The Chemical Effects of Alpha Particles and Electrons*, The Chemical Catalog Co., 1928, Amer. Chem. Soc Monograph No. 2. page 158. C. F. Hirshfeld, A. A. Meyer, L. H. Connell, *Study of the Mechanism of Cable Deterioration*, Detroit Edison Co., printed but not published by the Association of Edison Illuminating Companies, 1928, page 111.

that it is a complex hydrocarbon of high molecular weight. It is insoluble in all common organic solvents.

The gases produced by the discharge were pumped into the chamber *S*. Typical curves showing the pressure increase are given in Fig. 2, in which

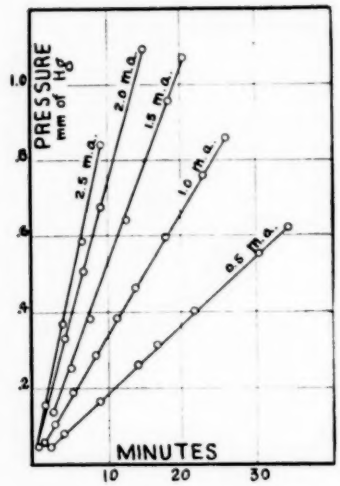

Fig. 2. Pressure-time curves for n-decane for various values of discharge current.

the time of duration of the discharge is plotted horizontally, and the pressure in *S*, vertically. Curves are given for five different values of discharge current from 0.5 to 2.5 ma., as indicated. The graphs are straight lines

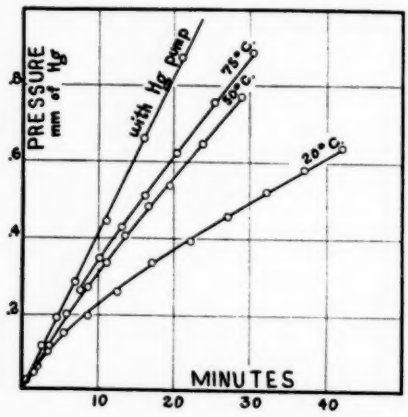

Fig. 3. Pressure-time curves showing effect of accumulation of reaction products on rate of reaction in n-tetradecane.

through the origin. Runs of a duration of 80 minutes showed no departure from this linear relationship. This is true in spite of the fact that at the begining of the run the electrodes were clean whereas at the end the cathode

was coated with a heavy layer of wax. It seems that the wax deposit on the cathode has no effect on the production of gas.[2]

A linear relation between pressure and time is not found unless the gaseous products are removed from the reaction chamber sufficiently fast. If the mercury pump P is not in operation the products will be removed from D only by the pumping action of the vapor stream flowing from E to T. In most cases this will not effect a complete removal. Fig. 3 shows graphs for n-tetradecane. The three curved lines were obtained with the liquid hydrocarbon held at 20°, 50°, and 70°C, as shown. The straight line was obtained with the pump P in operation. It can be seen that the curved lines have at the origin the same slope as the straight line, but their slope decreases as the

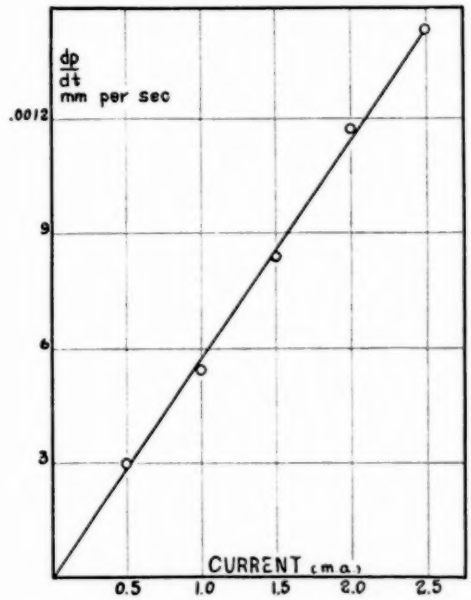

Fig. 4. Proportionality between discharge current and rate of reaction in n-decane.

discharge continues. This is probably due to the accumulation of reaction products in D, and consequent reverse reactions, or conduction of current by non-reacting ions. These hypotheses are supported by the fact that as the temperature of the liquid hydrocarbon is raised, and the rate of flow of vapor from E to T thereby increased, the pumping action of the vapor stream increases, the reaction products are more efficiently swept from D, and the curves approach closer to the straight line. A similar result was obtained with n-decane.

Plotting the slopes of the lines of Fig. 2 against discharge current, a straight line passing through the origin is obtained, as shown in Fig. 4.

[2] J. C. McLennan, M. W. Perrin, H. J. C. Ireton, Proc. Roy. Soc. **125,** 246 (1929), bombarded with cathode-rays a similar wax formed from acetylene and found no evidence of gas evolution.

The numerical data are given in Table I. This indicates that under the conditions of this experiment, the relation between current and rate of reaction is of the type,

$$dp/dt = ki \tag{1}$$

where k is a constant depending only on the kind of hydrocarbon, and i is the current. In other words it seems that conduction in gases may follow an electro-chemical equivalence law similar to Faraday's law of electrolytic conduction in liquids. It appears quite certain however, that the mechanism in the case of gases must be very different from that of electrolysis.

TABLE I. *Rate of production of gas in n-decane vapor for various values of discharge current.*

Current (m.a.)	$dp\ dt$ (−77°C)
0.5	0.000300
1.0	.000546
1.5	.000842
2.0	.001180
2.5	.001441

The rate of reaction has been found to be independent of pressure and the voltage between the electrodes. There is some evidence that it is independent also of the distance between the electrodes. These points are discussed somewhat more in detail below.

(1) *Effect of pressure.* Table II gives dp/dt for different pressures, with carbon dioxide cooling on the trap. It will be seen that dp/dt is constant,

TABLE II. *Rate of gas production and vapor pressure.*

Hydrocarbon	t°C	V.P. (mm Hg)	dp/dt (−77°C)
dodecane	0		0.000645
	22		640
n-decane	0	0.20	547
	22	1.25	555
	24	1.50	539
	40	4.50	533
n-octane	−15	.90	523
	0	2.95	511
n-heptane	−20	.63	800
	−17	.80	867
	0	11.45	816

within the experimental error, over a wide range of pressures, for a given compound. In the case of n-heptane the pressure change is over 1700 percent, whereas the corresponding change in dp/dt is only 2 percent. The vapor pressure data for dodecane were not available, but are probably similar to those of n-decane.

(2) *Effect of voltage.* Although it was not possible to determine the effect of different voltages by independently varying the potential difference between the electrodes, the automatic fluctuations in this quantity during the course of the runs served the purpose. These voltage changes were commonly as large as 25 percent yet no effect due to them was noticeable. The pressure-time curves were always straight lines as shown in Fig. 2. Hence it appears that if the current is held constant, the rate of reaction is unaffected by changes of potential difference between the electrodes.

(3) *Effect of electrode spacing and shape.* For the n-decane runs, two discharge bulbs were used, which were similar except that the distance between the electrodes was 5.5 cm in one and 8.5 cm in the other. The first gave as an average $dp/dt = 0.000546$, while the single run made with the latter gave $dp/dt = 0.000521$. Since the positive column was longer in the second case than in the first it can be concluded that in the case of n-decane any action which may occur in the positive column must be negligible in comparison with that occurring near the cathode.

As a further test of the locus of the reaction a point electrode about 1.0 mm in diameter and 1.0 cm long was substituted for the disk-shaped cathode. The electrode spacing was 8.5 cm. This gave $dp/dt = 0.000660$, an increase of about 27 percent over the rate obtained with the disk electrode. This indicates that the reaction goes to completion in the gas phase rather than on the electrode surface, but the difference is not sufficient to make the result conclusive.

Results similar to these have been obtained by a few other workers for other substances. Kirkby[3] studied the synthesis of water in the glow discharge and obtained a linear relation between current and amount of water formed. He also observed that most of the action occurred in the neighborhood of the cathode and that this was independent of pressure. Günther-Schulze[4] found the rate of reaction to be proportional to the current for the synthesis of water in the glow discharge for currents from 20 to 120 ma. The rate was independent of pressure. He found similar results for the synthesis of ammonia. A. Keith Brewer and J. W. Westhaver[5] have made an extensive study of the synthesis of ammonia, and also nitrogen dioxide. They also find proportionality between current and rate, and independence of pressure. They show that most of the reaction occurs in the neighborhood of the cathode and that it apparently goes to completion in the gas phase rather than on the surfaces of the walls or cathode.

The rates of gas production for each of the seven normal paraffin hydrocarbons are given in table III, and shown graphically in Fig. 5. These rates are for a current of 1.0 m.a. The subscripts -77 and -182 indicate the use of carbon dioxide and liquid air, respectively, as the refrigerant on the trap.

[3] P. J. Kirkby, Phil. Mag., [6] **7,** 223 (1904); **9,** 175 (1905); **13,** 289 (1907); Proc. Roy. Soc. **A85,** 151 (1911).

[4] A. Günther-Schulze, Zeits. f. Physik **21,** 50 (1924).

[5] A. Keith Brewer and J. W. Westhaver, J. Phys. Chem. **33,** 883 (1929); **34,** 159 (1930); **34,** 554 (1930).

TABLE III. *Rate of gas production for normal paraffins* (discharge current = 1.0 m.a.)

Hydrocarbon	Formula	dp/dt (−77°C)	dp/dt (−182°C)
n-pentane	C_5H_{12}	—	0.000208
n-hexane	C_6H_{14}	0.000757	.000173
n-heptane	C_7H_{16}	.000828	.000167
n-octane	C_8H_{18}	.000510	.000163
n-decane	$C_{10}H_{22}$	.000546	.000174
dodecane	$C_{12}H_{26}$	.000642	.000291
n-tetradecane	$C_{14}H_{30}$	.000702	.000346

The rates are expressed in mm of mercury per second increase in pressure in the storage chamber *S*.

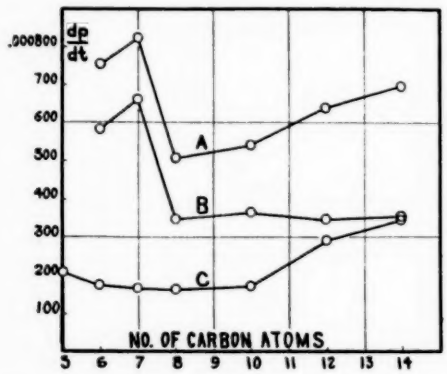

Fig. 5. Relation between molecular size and rate of reaction. Curves *A* and *C* represent data taken with carbon dioxide and liquid air respectively as refrigerants. Curve *B* was obtained by subtracting *C* from *A*.

In Fig. 5, curve *A* represents the rates of gas production with carbon dioxide cooling, curve *C* with liquid air cooling, while curve *B* was obtained by subtracting *C* from *A*. Although the writer has made no analyses of the gases collected, some idea of their composition may be obtained from these curves. Obviously they must be hydrocarbons or hydrogen. As was stated above, those having a vapor pressure greater than 0.1 mm at the temperature of the trap will pass through it, whereas those whose vapor pressure is less than 0.02 will be stopped. Hence the gases represented by curve *C* likely include hydrogen and methane, their vapor pressures being well above the limit. Ethylene, propylene and acetylene may also be present, for their vapor pressures, although not available for this temperature, may also be above the limit. Hirshfeld, Meyer, and Connell[6] have analysed the gases given off when liquid normal paraffins are rayed with cathode-rays from a Coolidge cathode-ray tube and found them to be made up of from 72 to 91 percent of hydrogen, 1.8 to 3.0 percent of methane, and 6.3 to 26.4 percent of undetermined light hydrocarbons. Reference to Fig. 5 will show that in a

[6] C. F. Hirshfeld, A. A. Meyer, L. H. Connell, *Study of the Mechanism of Cable Deterioration*, 1929. (See reference 1.)

gaseous electrical discharge a considerably smaller percent of hydrogen is obtained, curve *C* representing the maximum possible amount. On the other hand, the light hydrocarbons are present in larger amounts as shown by curve *B*. This may be due to the lower energy of the impacting electrons in the gaseous discharge. Or, it may be due to the longer period of bombardment in the cathode-ray experiments, in which the liquid hydrocarbons were exposed to the rays for periods of a few hours length. Polymerization and condensation may therefore have progressed further.

Heptane and hexane show a much greater production of light hydrocarbon gases than the others, as is shown by the hump in curve *B*. For these two substances the pressure-time curves (with carbon-dioxide as refrigerant) were not straight lines, as shown in Fig. 2, but broken lines each made up of two straight sections; the second section in each case was less steep than the first. This was due to the presence of hydrocarbon gases which condensed in the McLeod gauge, as soon as the difference in the mercury levels became equal to their vapor pressure at room temperature. The break for n-heptane occurred at a difference in mercury levels of about 120 mm, while that for n-hexane occurred at about 140 mm. No breaks in the pressure-time curves were found for any other substances.

Discussion

Previous work[1,5,7] indicates that chemical action in electrical discharge is initiated by positive ions. Once positive ions are formed the reaction appears to take place in one of two ways, (1) by a *chain mechanism* such as postulated by Bodenstein,[8] in which "there is formed an unstable intermediate product, rich in energy, which on further reaction gives rise not only to the final product, but also to another intermediate product which regenerates the same process again and again," or (2) by a *clustering process*, such as has been assumed by Lind in connection with his work on α-ray bombardment, and according to which positive ions attract surrounding neutral molecules forming an ion cluster which reacts chemically upon neutralization.

It seems that a satisfactory theory of chemical action in electrical discharge should be in harmony with the above hypotheses, and in addition should explain the following experimental facts: (1) proportionality between current and rate of reaction; (2) independence of rate of reaction on pressure; (3)occurrence of the greater part of the reaction in the neighborhood of the cathode. (These facts are supported not only by the work reported in this article but also by that of Kirkby, Günther-Schulze, and Brewer and Westhaver, mentioned above.)

A simple mechanism which meets these requirements is the following: Consider the electrons leaving the cathode. These traverse the cathode potential drop and thereby acquire energy which is expended in collisions in

[7] S. C. Lind, Science **67**, 565 (1928).

[8] Max Bodenstein, Chem. Reviews **7**, 2, 215 (1930).

the dark space and negative glow. We assume that the positive ions formed by these collisions serve as the initiators of the chemical action, giving rise to either chain or cluster processes.

Proportionality between current and rate of reaction will follow from this hypothesis if there is a constant ratio between the current and the number of positive ions formed in the dark space and negative glow. The existence of such a ratio seems quite likely for the ranges of pressure and current under consideration. Such a constant ratio would exist (1) if there were a constant ratio between the current and the number of electrons leaving the cathode, or in other words, between the number of electrons leaving and the number of positive ions arriving; and (2) if there were a constant ratio between the number of electrons leaving the cathode and the number of positive ions formed in the dark space and negative glow. Both of these assumptions are in good agreement with the generally accepted ideas of the glow discharge, and it seems likely that they are valid.

Independence of the rate of reaction of pressure can be explained by the relation $pd = \text{const.}$[9], where p is the pressure and d is the width of the dark space. From this it is clear that any change in pressure is compensated for by such a change in d that the amount of gas subjected to bombardment by electrons from the cathode remains constant. In other words, as the pressure changes the mean free path of the electrons changes so that the same number of collisions is made as before. Changes in pressure may be regarded as only magnifying or reducing the dimensions of the active region surrounding the cathode, but not affecting the total number of positive ions formed therein.

This picture disregards the action in the positive column. Any reaction which may occur there is probably due to the formation and recombination of ions which never reach the electrodes and hence have no relation to the current. In the experiments discussed here this action has apparently been small in amount, and could probably be made as small as desired by making the positive column sufficiently short.

The occurrence of the greater part of the reaction in the neighborhood of the cathode is obviously accounted for by this mechanism. It would be expected that the negative glow would be the seat of most of the reaction because of the high energy of the electrons and the high density of positive ions in that region.

Among the experimental results, which are not yet well-established, are: First, the apparent independence of reaction rate on electrode spacing, found in the case of n-decane. On the basis of the suggested mechanism this means only that in this case the amount of reaction in the positive column is negligible. Second, the independence of the reaction rate on voltage. It seems likely that the voltage fluctuations were caused by inconstant conditions on the wax-covered cathode surface. The cathode potential drop depends only on the nature of the gas, hence it must have remained constant, and thereby yielded a constant reaction rate regardless of the voltage across the electrodes.

[9] L. H. Dawson, Phys. Rev. **30**, 119 (1927).

The results presented in this article are not such as to distinguish between a chain and cluster mechanism. However, a cluster mechanism is indicated by the formation of the wax, which is apparently a hydrocarbon of high molecular weight such as would be formed by polymerization or condensation. It seems likely that these heavy molecules form on the surface of the cathode rather than in the gas phase, since such large clusters would probably be unstable in the gaseous state,[10] even though chemical forces were added to the ordinary forces of electrostatic induction between an ion and surrounding neutral molecules.

In conclusion the writer wishes to express his appreciation to those of the Departments of Physics and Chemistry of Cornell University who were helpful in this work, to Dr. H. A. Trebler for his interest in the problem and his valuable suggestions, and to Prof. Vladimir Karapetoff, who is in general charge of the above mentioned research program on insulation at Cornell University. He wishes especially to thank Mr. C. F. Hirshfeld, chief of research, and Mr. Alex Dow, president, both of the Detroit Edison Company, for the financial support which made the above described work possible, and for permission to publish the results.

[10] J. J. Thomson, *Conduction of Electricity Through Gases*, 3rd Ed., p. 66.

THE POLARIZED FLUORESCENCE OF SOLUTIONS OF RHODAMINE-B AND URANINE*

By Ernest Merritt and Donald R. Morey
Cornell University

(Received August 30, 1930)

Abstract

Measurements have been made of the extent of polarization in the fluorescence light from glycerine solutions of uranine and rhodamine-B. The results indicate that the fluorescence light is polarized to the same extent throughout any one fluorescence band; or, if there is a variation which these experiments have failed to detect, it cannot be much greater than one percent. These results thus confirm the observations of Wawilow and of Pringsheim and Wawilow. In the case of uranine the width of the fluorescence band is such that the frequency at the short-wave edge exceeds that at the long-wave side by more than twenty-five percent. The results therefore add support to the view that a fluorescence band is to be regarded as a unit. This view is still further strengthened by the fact that under some conditions of concentration there is evidence of the existence of two bands in the fluorescence spectrum of uranine, the polarization being constant throughout each band but different for the two bands.

If we adopt the usually accepted explanation of the cause of polarization in viscous solutions the results are best explained by the assumption that the duration of the fluorescence process is the same for all wave-lengths in a fluorescence band and that the duration is less for the small band of uranine than for the principal band. If this explanation is correct it may still be that the broad fluorescence band of uranine is really a group of overlapping lines; but if so the duration of the excited state is the same for all lines of the group. An alternative view, with which these results are altogether consistent, is that discussed by one of the writers in a previous paper, viz. that only a single electron transition is involved, and that the breadth and shape of the fluorescence band are determined by the disturbing effect of the solvent.

WHEN viscous solutions of the organic dyes are excited to fluorescence the emitted light is found to be partially polarized. The polarization is most marked when a solvent like glycerine is used, but it can be detected by sufficiently sensitive methods even in aqueous solutions. In its dependence upon the direction of observation and the direction of the electric vector of the exciting light this polarized fluorescence is qualitatively similar to the light scattered by small particles in the Tyndall effect.

All of the attempts that have been made to give a theoretical interpretation of the phenomena have involved two assumptions, namely: (1) that the active molecule is anisotropic, so that both the probability of excitation and the polarization of the emitted light are dependent on the orientation of the molecule; and (2) that the duration of the excited state is finite—or, in other words, that the act of emission requires an appreciable time. In solutions having small viscosity thermal agitation causes the orientation of the excited

* The investigation of which the work here described forms a part has been supported by a grant from the Hechscher Foundation for Research at Cornell University.

molecule to change so rapidly that the fluorescence light may be regarded as coming from molecules having a nearly random orientation and the polarization is small. In viscous solutions emission occurs before the molecules have had time to change their orientation and the polarization may be quite marked. In general, therefore, strong polarization of the emitted light indicates either large viscosity or short duration of the excited state. While there are difficult points that are not yet cleared up and seemingly contradictory experimental results that are yet to be explained this interpretation of the observed effects is in the main satisfactory.

The study of polarized fluorescence thus offers a means of obtaining information on two important points connected with radiation, viz., the symmetry of the molecule as exhibited in the processes of absorption and emission, and the duration of these two processes. So little is known about what goes on in a molecule while it is absorbing or emitting radiation, and the means by which we may hope to add to our knowledge are so few, that the study of polarized fluorescence would seem to deserve even greater attention than it has received.

The experiments here described were undertaken in the hope of determining by means of polarization measurements whether or not the duration of the fluorescence process is the same for different parts of the fluorescence band. If it is the same we should expect the emitted light to be polarized to an equal extent for all wave-lengths in the fluorescence spectrum. The results of previous experiments bearing on this point are contradictory. Weigert[1] found the polarization greatest at the red end of the fluorescence spectrum. Wawilow and Lewschin,[2] working with filters to separate different spectral regions, found the polarization practically the same throughout the spectrum. This result was later confirmed by Wawilow[3] for fluorescein and rhodamine by spectrophotometric measurements. With aesculin, both in sugar solutions and in solid gelatin, Pringsheim and Wawilow[4] found the polarization greatest at the short wave side of the band and least at the long wave edge, the value at the center of the band being intermediate between the two. On the other hand aesculin in glycerin showed nearly equal polarization throughout.

If the percentage polarization really does give an indication of the duration of the fluorescence process it is a matter of importance to reach a decision among these conflicting results, for such a decision would help in forming an opinion as to the type of emission process that is involved. Are we, for example, to treat the fluorescence of solutions as involving essentially the same processes as the fluorescence of gases, the observed differences being simply the result of the disturbing effect of the solvent? In some cases, notably that of benzene, this procedure certainly seems to be justified. If it is generally applicable, the broad and seemingly continuous fluorescence band of a substance like uranine must be thought of as being really a group of overlapping narrow

[1] F. Weigert, Phys. Zeits. **23,** 232 (1922).
[2] S. J. Wawilow and W. L. Lewschin, Zeits. f. Physik **16,** 135 (1923).
[3] S. J. Wawilow and W. L. Lewschin, Zeits. f. Physik **32,** 721 (1925).
[4] P. Pringsheim and S. J. Wawilow, Zeits. f. Physik **37,** 705 (1926).

bands which we have not yet been able to resolve. In this case the different parts of the emission band are due to different electron transitions and it would seem not unreasonable to expect the duration of the excited state to be different at different points in the spectrum. On the other hand it may be that the complexity of the active molecule and the enormous forces exerted on it by the solvent make necessary some new method of treatment. It has in fact been found that the disturbing effect of the solvent is sufficient, even if only one electron transition is involved, to account not only for the width of the band in the case of fluorescein and rhodamine but also for certain pecularities in the form of the absorption band and in the relation between fluorescence and absorption[5] There remains also the possibility that chemical action brought about by the exciting light is an important factor, possibly an essential factor, in the fluorescence of liquids and solids. While knowledge of the matter in which the polarization depends upon the wave-length cannot be expected to settle the question as to what line of attack should be followed it should at least be helpful.

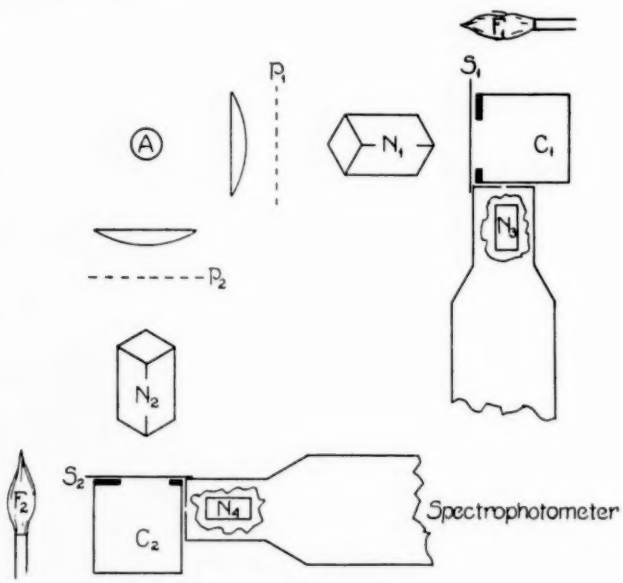

Fig. 1. Arrangement of apparatus.

EXPERIMENTAL

The arrangement of apparatus is shown in Fig. 1. The cells C_1 and C_2 containing identical solutions of uranine or rhodamine-B were placed before the two collimator slits of a large Lummer-Brodhun spectrophotometer. Fluorescence was excited in C_1 and C_2 by light from the mercury arc A, and the two fluorescence spectra were photographed at the same time and on the same plate. The blackening of the photographic plate was measured by a Moll

[5] E. Merritt, Phys. Rev. **28**, 684, (1926).

microphotometer, the two records being superposed, so that any differences could be readily detected. The two exciting beams could be polarized either in the horizontal or vertical plane by the nicols N_1 and N_2. Screens of blue glass, S_1 and S_2, cut out from the exciting beams nearly all light falling within the fluorescence band. There was enough transmission in the long wave region, however, and sufficient reflection from the cell walls, so that the strong lines 5461, 5770 and 5790 were frequently present in sufficient intensity to make a faint record on the photographic plate. In such cases they served as a check on the accuracy with which the two microphotometer records were superposed. To make certain that some check of this kind should be available sodium flames F_1, F_2 were placed in front of each collim-

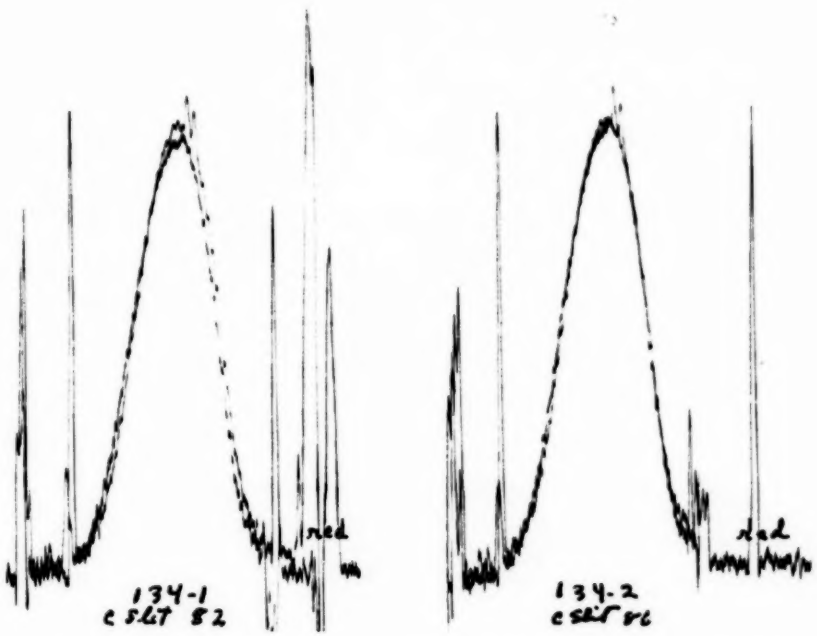

Fig. 2. Showing the effect of changing the opening of one spectrophotometer slit from 80 div. to 82 div., the other remaining unchanged.

ator, so as to have the sodium line show on the photographic plate. This wave-length is incapable of exciting fluorescence in the solutions tested. The screens S_1 and S_2 and the glass walls of the two cells proved to be so nearly free from strain that their depolarizing action was negligible. Analyzing nicols N_3 and N_4, were carried in the collimator tubes as shown.

Ordinarily the nicols N_1 and N_2 were both set so that the electric vector of the exciting light was in the vertical plane and were then left in this position. This procedure was made necessary by the fact that any change in the setting of N_1 or N_2 altered the distribution of the exciting light over the surface of the corresponding cell C_1 or C_2; and since the fluorescence light suffered absorption by the solution a slight change in the path of the fluores-

cence light through the solution was likely to result in an apparent change in the distribution of energy throughout the fluorescence band.

The adjustment was first tested by photographing the two spectra when both analyzing nicols (N_3 and N_4) were set with their principal planes horizontal. In this case the microphotometer records should be identical. Small inequalities in the intensity of the two bands were corrected by inserting pieces of clear glass in the path of one of the exciting beams at P_1 or P_2. The shapes of the bands were made similar by adjusting nicols N_1 and N_2 to make sure that the two beams of fluorescence light suffered equal absorption. The sensitiveness of the method varied from plate to plate, for the exactness with which the two curves could be made to coincide varied with the amount of grain structure fluctuations to be found on the microphotometer records. The time of exposure which made the density most sensitive to changes in intensity was determined roughly by trial. In Fig. 2, superposed microphotometer records are shown for a solution of rhodamine in glycerine, in one case when the two spectra were adjusted as nearly as possible to equal intensity and in the other when the width of one of the two slits was changed from 80 divisions to 82 divisions. From tests of this kind it seems safe to conclude that a change of 1 percent in the relative intensities of the two spectra could be detected with considerable certainty. There was no indication of errors due to variations in the emulsion from point to point; for after the two spectra were adjusted to equality exposures on different plates, or on different parts of the same plate, gave consistent results.

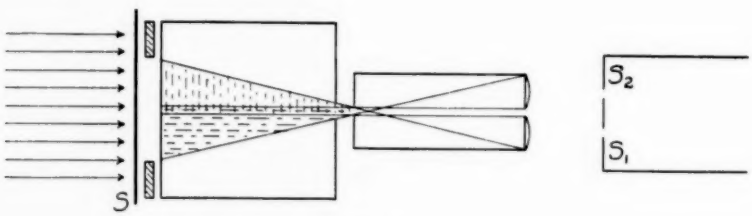

Fig. 3.

After the adjustment of the apparatus had been checked in this way one of the analyzing nicols was turned through 90° and the two bands were photographed again. By placing clear glass plates in the path of one of the exciting beams the intensities of the two bands were again made as nearly as possible equal. If the polarization of the fluorescence is the same for all wave-lengths it should be possible to bring the two microphotometer records into coincidence throughout the whole width of the fluorescence band.

To determine the actual magnitude of the polarization for the different solutions a Koenig-Martens spectrophotometer was used. Wawilow has described two methods by which the instrument may be utilized for such a determination,[6] both of which involve the assumption that the polarization of the light entering one slit is the same as that entering the other. This

[6] S. J. Wawilow, Zeits. f. Physik, **32,** 721 (1925).

makes it advisable to observe the fluorescence in the direction of the incident light (Fig. 3) rather than at right angles (Fig. 4); for we find that the fluorescence light originating at a greater distance from the exciting source shows less polarization than that excited in those parts of the solution that are nearer the source. Two causes probably contribute to this result, namely: (1)

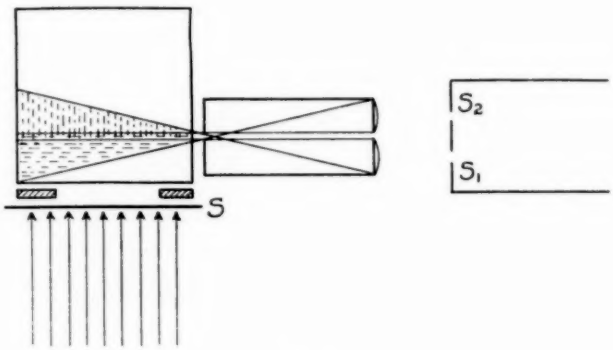

Fig. 4.

The longer wave-lengths in the exciting beam suffer greater absorption by the solution than do the shorter wave-lengths; so that the fluorescence from the front of the cell is excited by radiation whose average wave-length is longer than that of the exciting light which penetrates to the rear of the cell and excites fluorescence there. Since it has been shown experimentally that the percentage polarization becomes less as the wave-length of the exciting light is decreased,[7] we should expect the polarization to be greatest where the exciting light enters the cell. (2) The fluorescence originating in the rear of the cell is partly excited by fluorescence light from the front of the cell, which is at most about 35 percent polarized. This weakly polarized exciting light results in fluorescence with much less polarization than that of the rays producing it

The results of measurements made with the cell arranged as in Fig. 3 are given in Table I. For each solution the instrument was set on the middle of

TABLE I. *Results of measurements with cell arranged as in Fig. 3.*

Uranine in glycerine gms/cc	gm mol/liter	Method 1	Method 2	Average
10^{-3}	.0027	21%	23%	22%
10^{-4}	.00027	36	38	37
10^{-5}	.000027	34	41	38
$10^{-3}+10^{-2}$ Na_2CO_3		15	18	17
$10^{-4}+10^{-3}$ Na_2CO_3		25	27	26
$10^{-5}+10^{-4}$ Na_2CO_3		32	38	35

the fluorescence band and to gain intensity the slits were opened to 2 mm. No attempt was made to determine a possible variation of polarization

[7] P. Fröhlich, Zeits. f. Physik **35,** 193 (1926); W. L. Lewschin, Zeits. f Physik. **26,** 278 (1924)

throughout the band by the visual method. It will be noticed that the two methods give reasonably consistent results except for the most dilute solution. The differences probably result not so much from errors in setting as from a change in the distribution of the exciting light over the cell when the polarizing nicol is turned or removed.

Fig. 5. Rhodamine-B in glycerine. Comparison of fluorescence produced by unpolarized exciting light with that excited by polarized light having the electric vector vertical. Observed from the side.

RESULTS

Three solutions of uranine in glycerine (concentrations 10^{-3}, 10^{-4}, and 10^{-5} gr/cc) and one of rhodamine-B in glycerine (concentration 10^{-4} gr/cc) were tested in this way. In some cases the comparison was between the

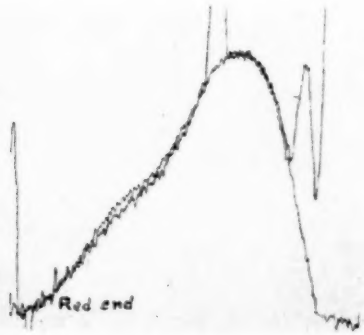

Fig. 6. Uranine in glycerine 10^{-5} gr/cc. Comparison of vertical and horizontal components of fluorescence produced by polarized exciting light.

fluorescence excited by unpolarized light and that observed when the excited light was polarized. In other cases the horizontally and vertically polarized components of the fluorescence light were compared.

For the rhodamine-B solution the fluorescence was found to be polarized to the same extent throughout the spectrum. The superposed microphotometer records for the polarized and unpolarized fluorescence are shown in Fig. 5.

In the case of uranine the microphotometer record sometimes showed a small band on the short wave-length side of the main band, probably corresponding to the similar small band found in the absorption spectrum. [See Fig. 6]. In the more concentrated solutions and in freshly prepared dilute solutions this small band did not appear. In neither band was there anything to indicate a variation of polarization with wave-length. The records indicate that the percentage polarization of the small band is distinctly greater than that of the principal band.

THE MOBILITY OF AGED IONS IN AIR

By Overton Luhr and Norris E. Bradbury
Physical Laboratory, University of California

(Received September 2, 1930)

Abstract

The mobility of air ions produced by x-rays has been measured by the simple Rutherford alternating current method. No change in mobility with age could be detected for ions aged as long as one second. The weighted average of the results gives 1.64 ± 0.05 and 2.25 ± 0.05 cm/sec per volt/cm for the mobilities of positive and negative ions respectively. No completely satisfactory explanation has been found for the continual decrease in the coefficient of recombination with age while the mobility remains unchanged. When moist air from the room was substituted for carefully dried air the mobility dropped to 1.4 and 1.8 cm/sec per volt/cm for positive and negative ions.

Introduction and Method

IT HAS been recently shown in this laboratory[1] that the coefficient of recombination of gaseous ions produced by an x-ray flash decreases continuously as the ions are aged for times between 0.001 and two seconds. The effect was noted not only for ions formed in air, but for ions formed in argon, nitrogen, and other gases. Moreover, since the effect continues long after the ions have attained random distribution in the gas, it would seem that, after the very rapid "initial recombination", some other aging effect must be involved. This aging effect might consist of the formation of heavy ion clusters and a weeding out of the smaller, faster ions by selective recombination.

In view of these unexpected results obtained in measurements of the coefficient of recombination, it was thought worthwhile to measure the mobility of ions which had been aged over periods of time varying between 0.01 and 1 second. The recombination apparatus which has previously been described by L. C. Marshall,[2] and one of the authors[1] was slightly modified by the addition of an extra brush to the commutator system, thus permitting measurements of mobility by the simple Rutherford alternating current method.[3] After the ions were formed by passing a flash of x-rays into the ionization chamber, they were allowed to age for various periods of time, and then drawn to the upper plate by an advancing potential applied through the commutator system. A bias of twenty percent or more was always maintained on the retarding potential to make sure that all the ions were removed before the conclusion of each cycle. In general, the aging periods, during

[1] O. Luhr, Phys. Rev. **35,** 1394 (1930); **36,** 24 (1930).

[2] L. C. Marshall, Phys. Rev. **34,** 618 (1929).

[3] J. J. Thomson, Conduction of Electricity Through Gases, p. 102, 3rd Edition Cambridge, 1928.

which the volume of ionization was field-free, were long compared to the time required to sweep the ions out by the field. This would allow clustering and selective recombination to take place under the same conditions as in the recombination measurements.

It may be noted that, to the authors' knowledge, mobility measurments have never before been made with ions older than 0.1 second. Moreover, x-rays have seldom been employed in mobility measurements of any kind, especially in later years, and no specific effect has been noted.

Results and Discussions

Figure 1 shows a typical series of curves for both positive and negative ions. The current in arbitrary units is plotted against the accelerating voltage and the straight part of the curves is extrapolated to the voltage axis.

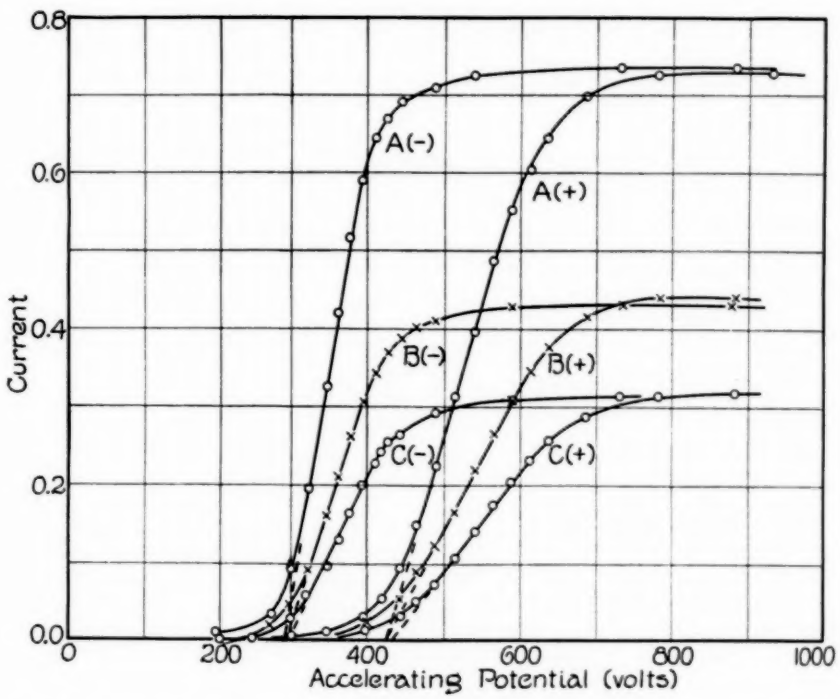

Fig. 1. Current plotted against voltage for negative and positive ions aged over periods of 0.06, 0.26, and 0.46 seconds for curves *A*, *B*, and *C* respectively. Extrapolation gives intercepts of 290 and 415 volts from which mobilities are calculated as 2.25 and 1.57 cm/sec per volt/cm for negative and positive ions.

The mobility is calculated from the relation $k = dD/VT$, where k is the mobility of the ions in cm/sec. per volt/cm, d is the distance from the volume of ionization to the collecting plate of the ionization chamber (5.9 cm), D is the distance between the plates (7.5 cm), V is the voltage at which the extrapolated line intercepts the axis, and T is the time the advancing voltage is applied.

The three series of curves, A, B, and C are for ions whose average ages were 0.06, 0.26, and 0.46 seconds respectively. These readings were all taken with the commutator revolving at the rate of one revolution per second, the setting being changed relative to the period of the x-ray flash to obtain the variation in age. The difference in saturation currents in the three cases shown represents the loss of ions by recombination during the time of aging. The mobilities obtained from the intercept points (415 volts and 290 volts) are: positive, 1.57; negative, 2.25. As can be seen from the figure, there is no evidence of the presence of more than one type of ion, or of any change in mobility with age which would result in different intercepts for the different curves.

The "asymptotic feet" obtained in every curve by this method throw a certain degree of uncertainty into the absolute value of the mobility. There is a sufficient straight portion in every case, however, to make the extrapolation quite certain, and better results can hardly be expected in a method of this kind where the volume of ionization is defined by the edges of an x-ray beam and where diffusion plays an important role.

The curves shown in Figure 1 are typical of a large number of runs, in which the age of the ions was varied between 0.01 and 1 second with commutator speeds of eight to one-half revolution per second. In no case was there any evidence of a decrease in mobility with age or of the presence of more than one type of ion. The weighted average of mobilities from some thirty runs was 1.64 for the positive ion and 2.25 for the negative. The results of each of the better runs fell within five percent of these values; so the absolute mobilities may be set at 2.25 ± 0.05 and 1.64 ± 0.05. These values are in close agreement with those obtained by Loeb,[4] Tyndall and Grindley, and other observers who have employed more accurate absolute methods.

In two cases values of the mobility markedly different from the average were obtained. The mobility was lowered to about 1.8 and 1.4 for negative and positive ions respectively when air from the room was substituted for the carefully purified air which had been passed through glass wool, sodium calcium hydrate, $CaCl_2$, P_2O_5, and liquid air traps. Such a result was to be expected as the effect of the presence of water vapor and other impurities in lowering the mobility is well known. The other case in which the value of the mobility differed considerably from the average was unexpected, and is probably worthy only of mention since the experimental conditions were very poor. If the driving field was low, and therefore the time of application long (i.e. slow commutator speed and long contact segment) the mobilities rose to values as high as three cm/sec for the negative ions and two cm/sec for the positive. In this case the driving field was of the order of ten volts/cm compared to fifty volts/cm when the best results were obtained. As conditions were the worst possible, with such factors as space charge, self-repulsion, and diffusion playing important roles, it is believed that the high values

[4] L. B. Loeb, International Critical Tables, Vol. VI, p. 110, New York, 1929.

obtained are spurious. As in the other runs, there was no indication of a change in mobility with age.

It remains to discuss the question: What property of the ions can change with age so that the coefficient of recombination may become continually lower, while the mobility remains unchanged? A change of mass resulting from cluster formation would decrease the coefficient of recombination which, on the J. J. Thomson theory,[5] is inversely proportional to the square root of the mass, but would not greatly affect the mobility which, according to the Langevin theory,[6] varies for mass as $[(M+m)/m]$,$^{1/2}$ a factor which at best could only decrease the mobility by a factor of the square root of two when the mass is increased from that of a single molecule to infinity. As it is probable that all ions have a mass considerably greater than that of a single molecule, it is very possible that an increase sufficient to reduce greatly the coefficient of recombination would not be detected in mobility measurements. However, such an increase in mass would very probably be accompanied by an increase of volume which must result in a shortening of the mean free path and a consequent decrease in the mobility proportional to that shortening. On the whole, the clustering and selective recombination hypotheses seem to be of doubtful tenability in the light of this experimental evidence. The solution to the problem may lie, then, in some change in the nature of the ion—possibly a redistribution of the electrical charge or a redistribution of the molecules in the cluster which makes the process of recombination more difficult, but does not change the mobility. Further speculation along this line is useless owing to a lack of definite knowledge concerning the nature of gaseous ions.

In conclusion, the authors wish to express their sincere appreciation to Professor Loeb for his guidance throughout the performance of these experiments.

[5] L. B. Loeb and L. C. Marshall, Jour. Frank. Inst. **207,** 371 (1929).
[6] L. B. Loeb, Kinetic Theory of Gases, p. 468, New York, 1927

ON THE ENTROPY OF HYDROGEN*

By D. Mac Gillavry

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Abstract

The entropy difference between ordinary hydrogen and hydrogen in perfect equilibrium, both in the solid phase at the absolute zero, has been calculated to be $(3/4)R \log 3+R \log 4$. This value checks the result given by Giauque and Johnston. The method is the direct evaluation along a reversible path of $\int dQ/T$ under certain idealized assumptions, using partition functions. The thermodynamical and statistical aspects are examined.

In a recent paper[1] I have indicated a theoretical way, by which the entropy difference between ordinary hydrogen and hydrogen in perfect equilibrium may be calculated. In this study I shall consider the details. With Fowler[2] I assume, that ordinary hydrogen is a mixture of para- and ortho-hydrogen in the fixed ratio 1:3, that thus transitions between para- and ortho-hydrogen do not occur in the ordinary mixture, and further, that para- and ortho-hydrogen and its different mixtures always have the same vapor pressure and the same heat of transition, so that the ratio 1:3 persists unchanged, when ordinary hydrogen is liquified or solidified. Recent experiments[3] have shown that this last assumption is not exactly true. Calculations made on these assumptions must be regarded, therefore, only as first approximations.

All earlier investigations and measurements have shown that ordinary hydrogen, gaseous, liquid or solid, may behave like a substance in true equilibrium. We now must add, provided the experiments are not continued over too long a time. One may speak of reversible quasistatic changes of state, and thus, the entropy difference of ordinary hydrogen at higher and lower temperatures can be discussed.[4] Going to rather high temperatures (above 500°C) the transition velocity becomes measurable, but at sufficiently high temperature we have again the proportion 1:3 anyway. It seems to me that there is no objection against idealizing the theory. Thus I suppose that the necessary experiments can be performed in such a short time, that the transition velocity may be regarded as negligibly small over the whole range of temperature. This concerns ordinary hydrogen.

* Contribution No. 635 from the Department of Chemistry, Columbia University, New York, N. Y.

[1] D. Mac Gillavry, Rec. trav. chim. **49**, 348 (1930).

[2] R. H. Fowler, Proc. Roy. Soc. **A118**, 52 (1928).

[3] K. F. Bonhoeffer and P. Harteck, Zeits. f. physik. Chem. Abt. B, **4**, 113 (1929); Naturwisscnschaften **17**, 182, 321 (1929). K. Clusius and K. Hiller, Zeits. f. physik. Chem. Abt. B, **4**, 158 (1929).

[4] P. Ehrenfest and V. Trkal, Verslag. Akad. Wetenschappen Amsterdam, **28**, 906 (1920).

On the other hand one can discuss also the entropy of hydrogen in ideal perfect equilibrium. In this second case care should be taken that the experiments are extended over such a long time, that the transition velocity may be considered as extremely rapid. Or one can take advantage of suitable catalysts accelerating this transition velocity.[5]

Now, the difference between para- and ortho-hydrogen resides only in the different rotational states. But the masses of all the hydrogen molecules are equal and the distribution of translational velocities is exactly the same. Further the total entropy can always be written as the sum of the translational and the rotational entropy, disregarding at first the vibrational states. If we take gaseous ordinary and gaseous ideal hydrogen at the same temperature (and pressure), then the difference in entropy must be a difference in rotational entropy only. Also, according to the assumptions already made by Fowler (l.c.), the difference in entropy between solid ordinary and solid ideal hydrogen must be rotational entropy only; for either form the rotations in the solid phase can be described by the same partition function, which holds good for the corresponding gas phase. The rotational entropy, therefore, should be unaffected by a change in phase, if it were rigorously true, that the ratio of ortho- and para-hydrogen is not altered by a change of phase, in the case of ordinary, as well as in the case of ideal hydrogen.

In this paper I shall calculate the entropy difference at the absolute zero between the two solid forms of hydrogen (ordinary and ideal). The problem may be solved in this way. One calculates at first the rotational entropy difference between ordinary hydrogen at a very high temperature and at the absolute zero. One calculates in the same way the rotational entropy difference of ideal hydrogen at the same very high temperature and at the absolute zero. Finally one goes to the limit of infinitely high temperature. But at infinitely high temperature there is no difference between ordinary and ideal hydrogen. The distribution of energy over the rotational states becomes exactly the same at extremely high temperatures. *Therefore, the desired difference of entropy is obtained by simply subtracting the two indicated differences.* At the same time it is obvious, that one may disregard complications caused by vibrations and other mechanisms. In the neighborhood of absolute zero rotational states only are excited.

For the actual calculation we can best make use of the methods developed by Fowler. Although ordinary hydrogen is a mixture, we can omit at once the paradox term, for the ratio of the two constituents is assumed to remain exactly constant. The entropy η is related to the partition function F by the equation:[6]

[5] K. F. Bonhoeffer and P. Harteck, reference 3. It is interesting to mention, that the catalysts, which catalyze the transitions between ortho- and para-hydrogen, also catalyze the combination of hydrogen and chlorine. Mellor in his Comprehensive Treatise on Inorganic and Theoretical Chemistry (Vol. II, page 159 top) says: "the mixed gases can be exploded by a piece of brick at 150°, while platinum black or charcoal may produce an explosion at ordinary temperature in the dark; in any case, they start the gases reacting—presumably by catalysis." Cf. Rec. trav. chim. **49,** 348 (1930).

[6] R. H. Fowler, Phil. Mag. **44,** 823 (1922).

$$\eta_2 - \eta_1 = \left| \left(R + RT\frac{d}{dT} \right) \log F \right|_1^2. \tag{1}$$

The indices 1 and 2 indicate two states with temperature T_1 and T_2; the pressure does not influence the rotational properties of perfect gases. The partition function of ideal hydrogen is:

$$F_i = 1 + 5e^{-6\sigma} + 9e^{-20\sigma} + \cdots + 3.3e^{-2\sigma} + 3.7e^{-12\sigma} + \cdots = \phi_p + \phi_o, \tag{2.1}$$

and the partition function of ordinary hydrogen is:

$$F_c = (1 + 5e^{-6\sigma} + 9e^{-20\sigma} + \cdots)^{1/4} \times (3.3e^{-2\sigma} + 3.7e^{-12\sigma} + \cdots)^{3/4} = \phi_p{}^{1/4} \cdot \phi_o{}^{3/4}; \tag{2.2}$$

and where ϕ_p is the partition function for para-hydrogen:

$$\phi_p = 1 + 5e^{-6\sigma} + 9e^{-20\sigma} + \cdots, \tag{3.1}$$

and ϕ_o is the partition function for ortho-hydrogen:

$$\phi_o = 3(3e^{-2\sigma} + 7e^{-12\sigma} + 11e^{-30\sigma} + \cdots). \tag{3.2}$$

$$\sigma = h^2/8\pi^2 IkT,$$

where h is the constant of Planck, k the constant of Boltzmann, I the moment of inertia. Thus, we have to form the expression:

$$\eta_c{}^* - \eta_i{}^* = \{\eta_c(0) - \eta_c(\infty)\} + \{\eta_i(\infty) - \eta_i(0)\}$$

$$= \lim_{T_2=\infty} \lim_{T_1=0} \left\{ - \left| R\left(1 + T\frac{d}{dT}\right) \log F_c \right|_1^2 + \left| R\left(1 + T\frac{d}{dT}\right) \log F_i \right|_1^2 \right\}. \tag{4}$$

The indices c and i indicate ordinary and ideal hydrogen respectively.

That the substitution of F_i for ideal hydrogen and of F_c for ordinary hydrogen in formula (1) gives correct results, can be proved also with the general theorems given by Fowler in his monograph on "Statistical Mechanics." One finds on page 129 the theorem. that any particular species of free molecule contributes to the characteristic function of Planck:

$$k\overline{M}\left\{ \log \frac{F(T)}{\overline{M}} + 1 \right\}, \tag{5}$$

where $\overline{M}$ is the average number present in the specified equilibrium state.[7] One gets the entropy from Planck's characteristic function by applying the operator $(1+T\,d/dT)$. Thus any entropy difference of ideal hydrogen, for instance, is given by:

$$\frac{\eta_{i_2} - \eta_{i_1}}{R} = \left| \left(1 + T\frac{d}{dT}\right) \left(\log \frac{F_i}{N} + 1 \right) \right|_1^2$$

[7] Combination of the two theorems on page 128 and 129.

$$= \left|\left(1 + T\frac{d}{dT}\right)\log F_i\right|_1^2 + \left|\log\frac{1}{N} + 1\right|_1^2$$

$$= \left|\left(1 + T\frac{d}{dT}\right)\log F_i\right|_1^2, \qquad (1)$$

then $\overline{M}$ here equals N, Avogadro's number, if we employ molar entropies.

It may be instructive to interpret ideal hydrogen also as a mixture of para- and ortho-hydrogen, between which two forms equilibrium has been established. One verifies easily that:[8]

$$\overline{M}_{pi} = \frac{\phi_p}{\phi_p + \phi_o} \times N \quad \text{and} \quad \overline{M}_{oi} = \frac{\phi_o}{\phi_p + \phi_o} \times N. \qquad (6)$$

We first get:

$$\frac{\eta_{i_2} - \eta_{i_1}}{R} =$$

$$\left|\left(1 + T\frac{d}{dT}\right)\left\{\frac{\phi_p}{\phi_p + \phi_o}\left(\log\frac{\phi_p}{\overline{M}_{pi}} + 1\right) + \frac{\phi_o}{\phi_p + \phi_o}\left(\log\frac{\phi_o}{\overline{M}_{oi}} + 1\right)\right\}\right|_1^2,$$

which becomes:

$$\left|\left(1 + T\frac{d}{dT}\right)\left\{\frac{\phi_p}{\phi_p + \phi_o}\log F_i + \frac{\phi_o}{\phi_p + \phi_o}\log F_i\right\}\right|_1^2$$

$$+ \left|\left(1 + T\frac{d}{dT}\right)\left\{\frac{\phi_p}{\phi_p + \phi_o}\left(\log\frac{1}{N} + 1\right) + \frac{\phi_o}{\phi_p + \phi_o}\left(\log\frac{1}{N} + 1\right)\right\}\right|_1^2$$

$$= \left|\left(1 + T\frac{d}{dT}\right)\log F_i\right|_1^2. \qquad (1)$$

The functions ϕ_p and ϕ_o depend on the temperature T.

I leave it to the reader to derive in an analogous way the formula for the entropy differences of ordinary hydrogen. I recall only that the concentrations of the para- and the ortho-forms now have the constant values:

$$(\overline{M}_p)_c = \lim_{T=\infty}(\overline{M}_p)_i = \lim_{T=\infty}\frac{\phi_p}{\phi_p + \phi_o}N = \frac{1}{4}N, \qquad (7.1)$$

$$(\overline{M}_o)_c = \lim_{T=\infty}(\overline{M}_o)_i = \lim_{T=\infty}\frac{\phi_o}{\phi_p + \phi_o}N = \frac{3}{4}N. \qquad (7.2)$$

The omission of the paradox terms from the two terms of equation (4) is legitimate, since they cancel if they are not omitted.

[8] Cf. R. H. Fowler, Statistical Mechanics, p. 30 formula (51), or p. 106 formulae (310) and (311).

Equation (4) represents exactly

$$\int \frac{dQ}{T} = \int d\eta = \int \frac{c_r}{T} dT,$$

the integral taken along the reversible way examined in this study. It must be possible to check the theory experimentally step by step, measuring heat capacities, as is always done. From the thermodynamical arguments used thus far it is evident, that no further term has to be added to the two terms of equation (4).

Now, we regroup the terms of expression (4) in a more convenient way, omitting the indices 1 and 2:

$$\frac{\eta_c^* - \eta_i^*}{R} = \lim_{T=0} \left(1 + T\frac{d}{dT}\right) \log \frac{F_c}{F_i} - \lim_{T=\infty} \left(1 + T\frac{d}{dT}\right) \log \frac{F_c}{F_i}. \qquad (4a)$$

We introduce two new functions, defined by the equations:

$$\phi_v = e^{-2\sigma} \phi_v',$$

$$F_c = (e^{-2\sigma})^{3/4} F_c' = e^{3\sigma/2} F_c';$$

and we substitute F_c' in the first term of (4a), noticing that always:

$$\left(1 + T\frac{d}{dT}\right) \log e^{-a/T} = \left(1 + T\frac{d}{dT}\right)\left(-\frac{a}{T}\right) = -\frac{a}{T} + \frac{a}{T} = 0;$$

thus:

$$\frac{\eta_c^* - \eta_i^*}{R} = \lim_{T=0} \left(1 + T\frac{d}{dT}\right) \log \frac{F_c'}{F_i} - \lim_{T=\infty} \left(1 + T\frac{d}{dT}\right) \log \frac{F_c}{F_i}.$$

I will give the results at once:

$$\lim_{T=0} \log \frac{F_c'}{F_i d} = \log 1^{1/4} \cdot 9^{3/4} = \log 9^{3/4}; \qquad (8.1)$$

$$\lim_{T=0} T\frac{d}{dT} \log \frac{F_c'}{F_i} = 0; \qquad (8.2)$$

$$\lim_{T=\infty} \log \frac{F_c}{F_i} = \log \left(\frac{1}{4}\right)^{1/4} \left(\frac{3}{4}\right)^{3/4}; \qquad (8.3)$$

$$\lim_{T=\infty} T\frac{d}{dT} \log \frac{F_c}{F_i} = 0. \qquad (8.4)$$

Thus:

$$\eta_c^* - \eta_i^* = R \log 9^{3/4} - R \log \left(\frac{1}{4}\right)^{1/4} \left(\frac{3}{4}\right)^{3/4} = \frac{3}{4} R \log 3 + R \log 4. \qquad (9)$$

The mathematical material, necessary for the justification of equations (8), has already been furnished by Fowler.[9]

This analysis is sound from a thermodynamical standpoint. However, a statistician may ask, does expression (4) really represent the desired entropy difference? Should not a third term be added? At higher temperatures ordinary and ideal hydrogen have the same internal energy and the same specific heat of rotation. At one time it has been supposed that transitions were prohibited, and at a later time it has been supposed that transitions do occur. Does not this different viewpoint necessitate a third term? Let us now add a third term, representing the entropy difference arising from those two viewpoints:

$$\eta_c(\infty) - \eta_i(\infty),$$

using again the most general theorems; then the operator

$$\mathrm{Lim}_{T=\infty} R(1+Td/dT)$$

has to work on the expression:

$$\frac{1}{4}\left(\log\frac{\phi_p}{N/4}+1\right)+\frac{3}{4}\left(\log\frac{\phi_o}{3N/4}+1\right)-\left(\log\frac{F_i}{N}+1\right)$$

$$=\log\phi_p{}^{1/4}\phi_o{}^{3/4}-\log\left(\frac{1}{4}\right)^{1/4}\left(\frac{3}{4}\right)^{3/4}+\left(\log\frac{1}{N}+1\right)-\log F_i-\left(\log\frac{1}{N}+1\right)$$

$$=\log\frac{F_c}{F_i}-\log\left(\frac{1}{4}\right)^{1/4}\left(\frac{3}{4}\right)^{3/4}.$$

The application of the operator $\lim_{T=\infty} R(1+T\ d/dT)$ yields zero,[10] in accordance with the thermodynamical considerations.

We may consider hydrogen as a mixture, if the experiments do not take much time, and we may consider hydrogen as a single gas, if we always wait a sufficiently long time. The entropy of hydrogen in equilibrium at higher temperatures can not depend on the length of time we keep it in a vessel. The equality can only be obtained in statistics by inserting the appropriate paradox terms (logarithmic terms), and for hydrogen considered as a mixture, and for hydrogen considered as a single gas; then the term representing the difference vanishes. Here we have a case, that a mixed gas has the same entropy as a single gas (see below).

Let us now consider the analysis more carefully. From thermodynamical considerations two terms have arisen:

$$\eta_c(0) - \eta_c(\infty) \quad \text{and} \quad \eta_s(\infty) - \eta_i(0).$$

To complete the argument from a statistical standpoint a third term has been added:

[9] One may refer concerning the limits (8.1) and (8.2) to Proc. Roy. Soc. **A118,** 52 (1928), and concerning the limits (8.3) and (8.4) to Statistical Mechanics p. 52, 53, and also Phil. Mag. **45,** 11 (1923).

[10] See equations (8.3) and (8.4).

$$\eta_e(\infty) - \eta_i(\infty).$$

In this way we have come to the equation:

$$\eta_e^* - \eta_i^* = \eta_e(0) - \eta_i(0) = \{\eta_e(0) - \eta_e(\infty)\} + \{\eta_e(\infty) - \eta_i(\infty)\} + \{\eta_i(\infty) - \eta_i(0)\},$$

which is trivial mathematically. It is obvious, that the mathematical calculation can at once be shortened in just this way, provided the general theorems are applied throughout. Therefore, we get:

$$\frac{\eta_e(0) - \eta_i(0)}{R}$$

$$= \lim_{T=0}\left(1 + T\frac{d}{dT}\right)\left\{\frac{1}{4}\left(\log\frac{\phi_p}{N/4} + 1\right) + \frac{3}{4}\left(\log\frac{\phi_o}{3N/4} + 1\right) - \left(\log\frac{F_i}{N} + 1\right)\right\}$$

$$= \lim_{T=0} \log\frac{F_e'}{F_i} - \frac{1}{4}\log\frac{1}{4} - \frac{3}{4}\log\frac{3}{4}. \tag{10}$$

Giauque and Johnston[11] give for this quantity

$$\eta_e^* - \eta_i^* = R\left(-\frac{1}{4}\log\frac{1}{4} - \frac{3}{4}\log\frac{1}{12}\right) = \frac{3}{4}R\log 3 + R\log 4, \tag{9a}$$

which is exactly our value. They consider ordinary hydrogen at the absolute zero as a mixture of para-hydrogen and of nine species of ortho-hydrogen, in accordance with the weight factor 3×3 of the lowest ortho-state. Although our final result is the same, Giauque and Johnston's interpretation of quantity (9a) as a paradox term does not seem *a priori* plausible. We do not compare ordinary hydrogen with the total of the separated constituents, but with 100% para-hydrogen. The conception of nine species of ortho-hydrogen is confined to the absolute zero, whereas our analysis, following Fowler, is generally applicable.

Fowler[12] gives the quantity $(3/4)R\log 9$, which value is not confirmed by the above given analysis. In fact, only the first term of expression (9) is given by Fowler. The second term, a paradox term, has resulted from our general *uniform* analysis. *This paradox term is intrinsic to entropy.* Its significance for diffusion problems constitutes only a special case.

In the monograph on Statistical Mechanics, page 163, one weight factor 3 is retained as an experiment, i.e., a correction $(3/4)R\log 3$ is used. The argument is, that nuclear weights must pursue hydrogen through all its combinations. If a nuclear spin accompanies hydrogen in all compounds, then I prefer to apply the full correction (9) to hydrogen and separate corrections to its combinations.

I am very much indebted to Dr. G. van Hasselt, Amsterdam, for many extensive discussions of the mathematical questions, and to Professor V. K. La Mer for the preparation of the manuscript.

[11] W. F. Giauque and H. L. Johnston, J. Am. Chem. Soc. **50**, 3221 (1928).
[12] R. H. Fowler, Proc. Roy. Soc. **A118**, 52 (1928).

A NEW RELATIVITY THEORY OF THE UNIFIED PHYSICAL FIELD

By William Band
Physics Department, Yenching University, Peping, China

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Abstract

This theory abandons the attempt to geometrise physics. Its aim is to give invariant differential equations of motion for mass-charge particles in regions where the indeterminacy of position and momentum is not significant.

Eddington's displacement rule is used to define an indeterminate vector field, and a simple generalisation of it is used to define an indeterminate tensor field. The vector field gives the possible velocity of a mass-charge particle at any point, and vector lines in the field are necessarily the tracks of the particle. The tensor field defines an invariant element of arc by means of which the orbit equations are given in the familiar parametric form.

Physical or actual fields are necessarily determinate functions and are defined by the variations of the indeterminate fields round closed loops in the usual way; but an alternative definition is suggested which does not depend upon such abstract processes. The usual identifications of the gravitation and electric field tensors give the classical laws for small fields. In the pure gravitation field the vector lines become Einstein's "geodesics", and for negligible gravitation field they become the empirical equations of motion of a charge in regions remote from atomic nuclei.

The theory is purely a descriptive apparatus, and its usefulness is definitely limited by the principle of indeterminacy. This admitted limitation enables the theory to avoid the inconsistency between field and atomic theory, an inconsistency which appears as merely the result of ignoring the limitation.

Introduction

ALL unified field theories have hitherto been attempts to geometrise completely the theory of the physical field: and such is the loyalty to the geometrical ideal that quite unintelligible properties are introduced such as non-integrable length and generalised parallel displacement. Such geometrical analogies are entirely useless as aids to imaginative conception[1] and therefore, in the writer's opinion, a hindrance to sound mathematics and to further progress. In the present theory geometrical interpretation is dispensed with. Stated briefly the aim of the theory is to derive a spacetime description of the motion of a material particle in regions where the indeterminacy in the particle's position and momentum is not significant; the motion being given by differential equations of invariant form.

Apart from Whitehead's theory[2] which does not appear to have attracted much attention, and which was based on the reactionary principle of absolute

[1] For a statement of the opposite view see Eddington's "The Mathematical Theory of Relativity" Art. 83.

[2] Dr. A. N. Whitehead, "The Principle of Relativity" Chaps. IV, V.

acceleration, the theory of O. Klein[3] appears to be the only theory which has succeeded in so deriving the equations of motion of charged particles in electric fields. Since the latter theory introduces an unknowable fifth dimension, it would seem less satisfactory than the present one which requires no such *ad hoc* hypothesis.

The writer has tried so to state the theory that it shall be obviously nothing more than a descriptive apparatus: not its validity, but only its usefulness as an apparatus depends upon the existence of the entities whose motions it proposes to describe. The limits to the usefulness of the method come out quite clearly when the fact of indeterminacy is taken into account. Thus the present theory will lead to the classical result that an accelerated electron must radiate energy, but it also contains the admission that such a result is meaningless when the acceleration is large and taking place in fields close to atomic nuclei. This seems to be a distinct advance on the classical theory, at least as usually stated; for no such admission is contained in the latter theory.

Thus the present theory suggests that the apparent inconsistency between the field theory and atomic theory is nothing more, in all probability, than a limitation in the usefulness of the field theory due to the fact of indeterminacy. Once the exact nature of this limited usefulness is defined the inconsistency evaporates.

I. The Vector Field of Possible Velocity

Begin with space time coordinates x_i, $i=1, 2, 3, 4$, and the fundamental array Γ_{jk}^{i} $i, j, k=1, 2, 3, 4$. The latter is composed of sixty four independent continuous single-valued functions of the coordinates.

Select arbitarily a 4-vector A^r at a definite point x_i and proceed by the rule

$$dA^r = -\Gamma_{si}{}^{r}A^s dx_i \tag{1}$$

to construct a vector field, by defining

$$A'^r = A^r + dA^r$$

at

$$x_i' = x_i + dx_i.$$

The field at any point will depend upon the track along which the rule (1) has been applied. We shall call this field the field of possible velocity, and use it to describe the motions of particles.

A vector line in this field will be a line, every element of which has coordinate components proportional to the components of the vector at the point; and so defined, will be the track of a particle with the corresponding initial conditions. The equations of a vector line follow immediately from Eq. (1) as

$$d^2x_i = -\Gamma_{jk}{}^{i}dx_j dx_k. \tag{2}$$

This is a set of four differential equations of the second order, their solutions containing eight arbitrary constants, the four components of initial velocity and the coordinates of the starting point.

[3] O. Klein Zeits. f. Physik **46**, 188 (1927).

II. The Fundamental Tensor Field

Erect, again at any initial point, the (symmetrical tensor) components a_{ik} and just as in §1, define a tensor field by

$$\begin{aligned} da_{ik} &= (a_{rk}\Gamma_{is}{}^{r} + a_{ir}\Gamma_{ks}{}^{r})dx_s \\ -\,da^{ik} &= (a^{rk}\Gamma_{rs}{}^{i} + a^{ir}\Gamma_{rs}{}^{k})dx_s \end{aligned} \tag{3}$$

where a^{ik} is the usual normalised subdeterminant of a_{ik}.

An associated covariant vector

$$A_i = a_{ik}A^k$$

may be defined at any point, and combining Eqs. (1) and (3) shows

$$dA_i = \Gamma_{is}{}^{k}A_k dx_s. \tag{1'}$$

Provided we remember that Eqs. (3) are not integrable, and that therefore the double partial differentiation of the a_{ik}'s is non-commutative, they can be expressed in the form

$$\partial a_{ik}/\partial x_s = a_{rk}\Gamma_{is}{}^{r} + a_{ir}\Gamma_{ks}{}^{r} \text{ etc.} \tag{3'}$$

Insert these equations in the usual definition of the Christoffel three-index symbol of the second kind, we deduce that, if we put

$$\Delta_{jk}{}^{i} = \tfrac{1}{2}(\Gamma_{jk}{}^{i} + \Gamma_{kj}{}^{i}) \tag{4}$$

$$\nabla_{jk}{}^{i} = \tfrac{1}{2}(\Gamma_{jk}{}^{i} - \Gamma_{kj}{}^{i}) \tag{4'}$$

then

$$\left\{ij,\ k\right\} = \Delta_{ij}{}^{k} + a_{ri}a^{ks}\nabla_{sj}{}^{r} + a_{rj}a^{ks}\nabla_{si}{}^{r}. \tag{5}$$

Using Eqs. (4), (4'), and (5), Eq. (2) becomes

$$d^2x_i + \left\{jk,\ i\right\}dx_j dx_k = 2a_{rj}a^{is}\nabla_{sk}{}^{r}dx_j dx_k. \tag{2'}$$

III. Fundamental Invariants

If we define invariant

$$A^2 = A_s A^s$$

we can show by Eqs. (1) and (1') that the value of A is a constant independent of position, depending only on the initial values of A_s, A^s. Similarly if we define the invariant

$$ds^2 = a_{ij}dx_i dx_j \tag{7}$$

and apply the rule of association

$$d\cdot dx_k = -\,\Gamma_{ij}{}^{k}dx_i dx_j \tag{1''}$$

the value of ds will also be a constant depending only on the initial values of the displacement ds_i and the tensor a_{ij}. Comparison of Eqs. (1'') and (2)

shows that we may therefore use ds as an invariant differential to give the Eqs. (2) the form

$$d^2x_i/ds^2 + \Gamma_{jk}{}^i dx_j/ds dx_k/ds = 0. \tag{8}$$

Since ds is an invariant for coordinate transformations, we may use the variation equation

$$\delta \int ds = 0$$

to deduce[4] the tensor character of the expression

$$d^2x_i + \{jk, i\} dx_j dx_k = t^i \tag{10}$$

and as usual also the tensor

$$D^{ij}{}_{,k} = \partial D^{ij}/\partial x_k + \{sk, i\} D^{sj} + \{sk, j\} D^{si}. \tag{11}$$

and the similar derivatives of tensors of different order.

Note that although (10) is a tensor at any point, it is not a determinate function of position; solutions of (9) are not fixed by the initial conditions, as are those of Eq. (2).

IV. Actual Physical Fields

We have introduced the idea of a possible field, indeterminate at any point, but actual fields will be determinate at every point. Such fields may be obtained from the fundamental array in the usual way.

Thus the total change in the possible vector field on going round a closed space-time track is[5]

$$\Delta A^i = -\tfrac{1}{2} \iint {}^*B^i{}_{jrs} A^j dS^{rs} \tag{12'}$$

and similarly the change in the tensor field is[6]

$$\Delta a_{ij} = -\tfrac{1}{2} \iint (a_{kj} {}^*B^k{}_{irs} + a_{ik} {}^*B^k{}_{jrs}) dS^{rs} \tag{12''}$$

where

$${}^*B^r{}_{ijk} = -\partial \Gamma_{ij}{}^r/\partial x_k + \partial \Gamma_{ik}{}^r/\partial x_j + \Gamma_{ik}{}^s \Gamma_{sj}{}^r - \Gamma_{ij}{}^s \Gamma_{sk}{}^r \tag{12}$$

is a tensor determined by the array.

Define as usual

$${}^*R_{ij} = {}^*B^r{}_{ijr} \tag{13}$$

$${}^*G_{ij} = \tfrac{1}{2}({}^*R_{ij} + {}^*R_{ji}) \tag{13'}$$

[4] For an alternative deduction of the tensor character of (11) see the writer's "Mathematical Properties of a Continuum with Indeterminate Metric" shortly appearing in the P. R.S.

[5] See Eddington, reference 1, Art. 92.

[6] The proof of this is analogous to that of the preceeding equation.

and

$$*F_{ij} = *B^{r}{}_{rij} \tag{13''}$$

Then by Eq. (12) we can show that

$$*F_{ij} = \partial\Gamma_{si}{}^{s}/\partial x_j - \partial\Gamma_{sj}{}^{s}/\partial x_i \tag{14}$$

or that

$$*F_{ij} = *K_{i,j} - *K_{j,i} \tag{14'}$$

where

$$*K_i = \Gamma_{si}{}^{s} + \partial f/\partial x_i \tag{14''}$$

in the original coordinates, but transforms as a vector; f being any function of position, invariant.

An alternative antisymmetrical tensor[7] may also be defined by

$$*H_{ij} = *K'_{i,j} - *K'_{j,i} \tag{15}$$

where

$$*K_i' = \nabla_{is}{}^{s}. \tag{15'}$$

In what follows no difference results from using $*H_{ij}$ instead of $*F_{ij}$.

(a). Pure gravitation field.

Let us limit our choice of the 64 array-components at any point by the twenty-four independent equations

$$\nabla_{jk}{}^{i} = 0. \tag{16}$$

Then Eqs. (4'), (4) and (5) show that Eq. (12) reduces to the classical Riemann-Christoffel tensor, both (15) and (13'') vanish, and (13') becomes Einstein's symmetrical field tensor. By virtue of (12'') the components a_{ij} become determinate functions of position, Eqs. (3) becoming mere identities. In this case therefore our theory is simply a restatement of Einstein's from a new point of view; the vector lines or particle orbits, becoming Einstein's so-called geodesics.

(b). Negligible gravitation field.

We wish to study the field of a small charged particle, in particular, of an electron. The gravitation field of an electron may be neglected[8] to a first approximation, and if zero external gravitation field is taken then we may take the three index symbols as zero both in the orbit Eqs. (2') and in the derivatives (11).

Maxwell's first set of laws

$$\partial F_{ij}/\partial x_k + \partial F_{jk}/\partial x_i + \partial F_{ki}/\partial x_j = 0 \tag{17}$$

are identically satisfied if either (14) or (15) are used as the electric field tensor; and his second set

$$J^{i} = \partial F^{ij}/\partial x_j \tag{17'}$$

[7] For proof (of tensor nature) refer to the paper mentioned in reference (4) above.

[8] See Eddington, reference 1, Arts. 78, 80.

are satisfied to the degree of approximation assumed, if we define

$$J^i = {}^*F^{ij}{}_{,j}. \tag{18}$$

Again we have approximately

$$\partial^2 D_i/\partial x_j \partial x_k = D_{i,jk} = D_{i,kj}$$

so that by (14′) and (18)

$$J_{i,j} = a^{rs}({}^*K_{i,r} - {}^*K_{r,i})_{,js} = a^{rs}({}^*K_{i,jrs} - {}^*K_{r,sij})$$

or

$$J_{i,j} - J_{j,i} = a^{rs}({}^*K_{i,j} - {}^*K_{j,i})_{,rs}$$

giving

$$a^{rs}{}^*F_{ij,rs} = J_{i,j} - J_{j,i} \tag{19}$$

A solution of this[9] is

$${}^*F_{ij} = (1/4\pi)\iiint (1/r)(J_{i,j} - J_{j,i})dv \tag{20}$$

which gives the field at distance r from the volume dv containing the current density J_i. Suppose the current $J_i dv$ is due to a charge e moving with a velocity A_i, then $J_i dv = eA_i$, so that Eq. (20) becomes

$${}^*F_{ij} = (1/4\pi)(e/r)(A_{i,j} - A_{j,i})$$

or, by (1′) and (4′)

$${}^*F_{ij} = 2\nabla_{ij}{}^k A_k e/4\pi r. \tag{21}$$

If the charge e is not considered a point singularity, it must be supposed to be such that each element has the same velocity, and Eq. (21) to have been integrated over the volume dv containing e.

Construct any sphere of radius a completely enclosing the charge e; then it is easy to show that the average of the values of de/r at all points over the surface of the sphere is de/a, so that the average of e/r is also e/a, and the average of the field taken over the surface of the sphere will therefore be

$$F_{ij}' = \frac{e}{4\pi a} 2\nabla_{ij}{}^k A_k. \tag{21′}$$

Suppose now that the external field varies only so slowly that its variation over the sphere of radius a can be neglected, then we may assume that it is possible to choose the sphere so that the external field F_{ij}'' is equal and opposite to the average F_{ij}'; this sphere will be defined as the boundary of the charged particle, or even as the particle itself. Actually the sphere is only an approximation: a more accurate definition would be the surface, assumed to exist, over which the external field just balances the corpuscle's field at every point.

[9] See Eddington, reference 1, Arts. 72, 74.

Granting this assumption,[10] that the particle is bounded by a surface of zero field, the equations of motion of the charge e are given by putting in (2′)

$$a_{rj}dx_j/ds = A_r,\ dx_k/ds = A^k,$$

and

$$2\nabla_{sk}{}^r A_r = (4\pi a/e)F_{sk}{}' = -(4\pi a/e)F_{sk}{}''$$

giving, of course with the approximation mentioned before,

$$m = e^2/4\pi a,\ md^2x_i/ds^2 = -eA^rF_r{}''_i \tag{22}$$

which, if m be interpreted as the mass of the particle, are the empirical equations of motion of charged particles, in regions where the field $F_{ij}{}''$ is not sensibly varied over the volume occupied by the charge.

V. The Principle of Indeterminacy

Heisenberg's principle of indeterminacy shows that the vector line method cannot give anything more than an approximate description of phenomena, for to do so it requires an exact knowledge of the initial conditions. The degree of approximation can be roughly estimated, however.

Let q, p be a typical pair of coordinates and momentum components actually measured as the initial conditions of the particle, and let the estimated uncertainties be Δq, Δp; definite values satisfying

$$\Delta q \cdot \Delta p = 0(h). \tag{23}$$

Describe a sphere of diameter D and centre q, where

$$D > \Delta q, \text{ and } D - \Delta q = 0(\Delta q). \tag{24}$$

If this sphere is moved so that its centre follows the track found by putting the measured initial conditions in (22), then the particle will certainly remain within the sphere for a finite time T. The greater T or the smaller Δq and D, the more useful the vector line description, and vice versa. We must be careful not to assert that if exact initial conditions could be found, then Eqs. (22) would give an exact description of the motion; for such an assertion can never be experimentally verified. Essentially, therefore the time T must be determined experimentally in every case; it is not possible to deduce from the purely abstract descriptive apparatus any binding limits to its applicability; an appeal to experiment must be made.

Nevertheless the following argument which, for the above reasons, cannot claim to be rigorous, may not be without interest.

In zero external field, (that is zero after the initial measurements have been made) an electron obeying Eq. (22) will move with its initial velocity unchanged. Any initial discrepancy between its measured and its "actual"

[10] Eddington's assumption (reference 1, Art. 80) that the two fields neutralise each other throughout the volume occupied by the charge could be used here just as well, but the one given in the text seems to be a useful alternative.

velocity will be transmitted as it were along its motion unchanged. Hence the time T in which the electron may drift out of the sphere of diameter D mentioned above will be

$$T = (D - \Delta q)/\Delta v$$

or by Eq. (23)

$$= (m/h)(D - \Delta q)(\Delta q) \tag{25}$$

For the electron $(m/h) = 0(1)$ so that by Eq. (24)

$$T = 0(\Delta q^2).$$

Suppose the initial velocity is measured as 10^8 cm/sec; and allow an uncertainty of no more than 10^3 cm/sec. Then by Eq. (23) the uncertainty in the initial position will be of the order of 10^{-3}cm. Thus T is of the order of 10^{-6} sec. and the length of track traversed in that time of the order of 100 cm.

When the field is not zero the initial discrepancy is not transmitted unchanged and the value of T becomes correspondingly uncertain, in general less. When the field varies so rapidly with position that it is sensibly different for different points within the sphere D, the various possible tracks starting from the points of Δq will in general diverge so rapidly that the sphere D will contain them only for a uselessly short time.

This non-rigorous argument thus leads us to suspect that in regions near atomic nuclei, where the space-variation of the field is great, the vector line method becomes useless; a result which is in full agreement with experimental data.

Independent of this argument is the further possibility that in the non-uniform fields near atomic nuclei, the boundary of the electron as defined in §4 can no longer exist. In this case the electron would cease to function as a particle and the process of deriving Eqs. (22) would no longer be possible.

LETTERS TO THE EDITOR

Prompt publication of brief reports of important discoveries in physics may be secured by addressing them to this department. Closing dates for this department are, for the first issue of the month, the twenty-eighth of the preceding month; for the second issue, the thirteenth of the month The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents.

Effect of Electric Field upon X-ray Diffraction Pattern of a Liquid

McFarlan's small positive effect (Phys. Rev. **35,** 1469 (1930) of an applied electric field on the x-ray diffraction halo of nitrobenzene is both interesting and important. He finds a definite increase of intensity at the maximum in the halo. He evidently favors the following suggestion: "The effect of the field is to bring about a more orderly arrangement of the molecular scattering centers with an increased regularity in the spatial distribution of these centers."

Attention should be called to the view that the nitrobenzene has a group structure without the electric field, and that the field, acting on the relatively large electric moment of each group, caused a change in the number of groups per unit volume oriented at any angle. The second is more acceptable for the following reasons:

(a) The existence of the semi-orderly, temporary groups (cybotaxis) accounts most readily for the numerous experiments in x-ray liquid diffraction in this laboratory and elsewhere.

(b) There is no reason to anticipate that the applied electric field would be powerful enough to alter the internal regularity of a group. McFarlan's computation on the effect on a single independent molecule shows that its orientation is negligible.

(c) Similarly there is not sufficient reason to anticipate that the applied electric field would increase the size of the individual groups, and one could not be certain that such an increase would result in an increase in intensity, for the groups are imperfect and cannot be treated as small crystals.

(d) The effect of the electric field would be noticeable on these groups on account of the large value of the moment. Indeed, from McFarlan's experiments one can estimate the size of these groups, if one assumes either a permanent or an induced electric moment.

(e) The adoption of the group view explains both the original diffraction effect and the change caused by the field. As already said, it seems to the writer that the second view is much more plausible.

I may be permitted to emphasize McFarlan's suggestion that "the effect just described is not associated with the Kerr effect." An illustration may be given of the vast difference in similar optical and x-ray effects. Para-azoxyanisol in the liquid crystalline and, at higher temperatures, the transparent states, gives practically the same x-ray diffraction effect, though one is optically anisotropic and the other isotropic. The optical effects do not require crystallinity in the x-ray sense.

G. W. STEWART

University of Iowa
September 17, 1930

Interpretation of the Spectra of CaF and SrF

In the course of a search for isotope effects in the band spectra of the alkaline earth fluorides, we have obtained high dispersion spectrograms of the visible CaF and SrF bands in both emission and absorption. With CaF, the faint bands expected for $Ca^{44}F$ could not be observed, as they would in all cases be masked by the $Ca^{40}F$ system. The SrF bands, however, are favorably placed for the detection of the lighter isotope, Sr^{86}, and we have identified several $Sr^{86}F$ heads accompanying the main $Sr^{88}F$ heads in the $(v+1, v)$ sequence of the yellow-green system. They lie to the violet of the main heads, the

average isotopic displacement of the first six members being 0.92 cm^{-1}. The mean deviation of observed from calculated displacements is only 0.03 cm^{-1}, and no trend is evident. By visual estimates the relative intensity of the $Sr^{86}F$ to the $Sr^{88}F$ bands is considerably below that predicted by the calculated abundance ratio, 1 to 5.5. Combined with a similar observation by Aston[1] with the mass-spectrograph, this indicates either an exceptionally large packing fraction for Sr, or an error in the accepted atomic weight.

By comparing these spectra in emission and absorption, we are able to draw conclusions about the rotational structure of the bands, direct measurement of which cannot be hoped for, even with a large grating. The green and red systems of CaF, and their analogues in SrF, have been ascribed by Johnson[2] to transitions $^2\Sigma \rightarrow {}^2\Sigma$ and $^2\Pi \rightarrow {}^2\Sigma$ respectively. Our results support these designations, but disagree with Johnson in several important respects. The near equality of rotational constants in the upper and lower states causes the heads to be formed at a very high value of J, at a considerable distance from the band origins. In this case data on the heads cannot give reliable values of the vibrational constants, since the distance from head to origin is not even approximately constant throughout the system. By assuming that the combination principle can be applied to measurements of the heads to find accurate values of the vibrational term-differences, Johnson has been led to wrong assignments of quantum numbers in the sequences $^2\Sigma^{(v+1)} \rightarrow {}^2\Sigma^{(v)}$ and $^2\Pi^{(v)} \rightarrow {}^2\Sigma^{(v+1)}$ in CaF. Furthermore, the value of J_{head} is so large in some cases that heads do not appear at the temperature of the arc, a fact which explains Johnson's failure to observe certain sequences. The remarkable difference in the appearance of the $^2\Sigma \rightarrow {}^2\Sigma$ systems in emission and absorption[3] can be readily interpreted as a temperature effect of the usual type if the double heads are ascribed not to R and Q branches, as suggested by Johnson, but to a doublet R branch, probably representing a very large ρ-type doubling.

Estimates of the molecular constants of CaF have been made from partial measurements of the fine structure, using formulas for the separation of the P and Q heads in the red system. The moment of inertia in the lower state is about $I_0'' = 86 \times 10^{-40}$, and is very nearly the same in the upper states. Johnson's interpretation of the heads in the $^2\Sigma \rightarrow {}^2\Sigma$ system, besides being incompatible with their appearance in absorption, leads to unreasonable values of the constants, since he places the origin (Q head) of the (0, 0) band only 6.5 cm^{-1} from the R head. Using our approximate values of the rotational constants, the various unusual features of the band systems can be shown to be a necessary consequence of the type of structure postulated. Details of this work will be published elsewhere.

A. HARVEY,
F. A. JENKINS

Department of Physics
University of California
September 25, 1930

[1] F. W. Aston, Nature **113,** 856 (1924).

[2] R. C. Johnson, Proc. Roy. Soc. **122A,** 161 (1929).

[3] O. H. Watters and S. Barratt, Proc. Roy. Soc. **118A,** 120 (1928).

Structure of *K*-radiation from C, B, and Be

In the "Physical Review" for the 15th of July Mr. L. Y. Faust has published the results of his research upon the structure of the softest K-radiation. He finds that the lines of carbon, boron and beryllium consist of a number of components, whose relative intensity varies with the angle of incidence and the tension. In order to confirm this statement I have microphotometered several lines of the carbon, boron and beryllium spectra, obtained with the special x-ray gratings ruled in this laboratory.[1] The results of this investigation will be published in the "Zeitschrift für Physik." Though the dispersion is greater than that used by Mr. Faust and the resolving power of the microphotometer probably is larger, the blackening curve appears quite even in its course. Nothing corresponding to the components found by Mr. Faust was observed. Moreover the total blackening lies within a considerably smaller range of wave-length. By way of example Mr. Faust finds 9 components in the

[1] M. Siegbahn and T. Magnusson, Zeits. f. Physik **62,** 435 (1930).

carbon line, extending over the range from 43 to 48A, while the carbon lines on my plates are only about 1A wide. The cause of variance in the results obtained is probably due to inaccuracies in the gratings used by Mr. Faust. As has been pointed out by Dr. Fagerberg[2] even very small variations in the grating constant can give rise to considerable errors in the structure of the lines.

MARTIN SODERMAN
Physical Laboratory,
University of Uppsala,
September 12, 1930

[2] S. Fagerberg, Zeits. f. Physik **62**, 457 (1930).

High Efficiencies of Emission from Oxide-Coated Filaments

Very high efficiencies of electron emission from oxide coated filaments have been observed. Inasmuch as these observations were made in connection with an entirely different problem, no complete investigation has been made as yet on this subject. The observations are here reported as being of interest in connection with emission phenomena.

The filaments were of nickel, coated with barium and strontium carbonates. They were given a conventional exhaust and activation.

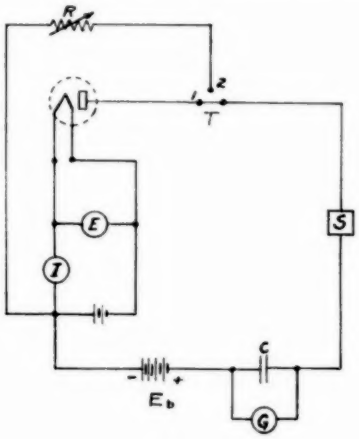

Fig. 1.

The method of measuring emission is illustrated in Fig. 1. The filament is heated to the proper temperature and the voltage E_b applied. With the switch T in position 1 the contactor S is operated. This contactor closes the circuit for a very short time (of the order of 10^{-3} second) during which time the emission current charges the condenser C. The deflection of the galvanometer G is read. Then the switch T is thrown to position 2 and the non-inductive resistance R adjusted until operating contactor S gives the same galvanometer deflection as before. The emission is then E_b/R. This method was adopted so that the full saturation emission could be drawn without the filament temperature being changed appreciably.

At normal operating temperatures efficiencies of from one to four amperes per watt were obtained. These figures represent the range of a considerable number of filaments presumably operating at the same temperature. It should be pointed out that these observations were made on filaments representative of a large number, and that no special care was exercised to secure high activity in those tested. These results were checked by means of the standard power-emission chart. Readings were taken of emission in the usual way of applying a continuous potential to the anode at such low temperatures that the emission could not appreciably affect the filament temperature, and the curves extrapolated to determine the emission at normal temperature.

Fig. 2 shows the results obtained by the two methods. The agreement is as close as may be expected, since neither method gives exactly uniform results on the same filament at different times, due either to errors of measurement or to changes in the emission of the filament.

Fig. 3 shows the emission per square centimeter plotted against watts per square centimeter for representative filaments.

The temperatures of the filaments were determined by means of an optical pyrometer, and checked by computation from the watts per unit area and the probable thermal emissivity of the surface. From Dushman's equation[1]

$$I = A T^2 \epsilon^{-b_0/T}$$

the values of b_0 and A were computed from the temperatures and emissions. On a representative filament, values of b_0 between 8,700 degrees and 10,500 degrees were computed. The value of A was about 0.3 ampere per

[1] S. Dushman, Phys. Rev., Vol. 21 No. 6, p. 623, June, 1923.

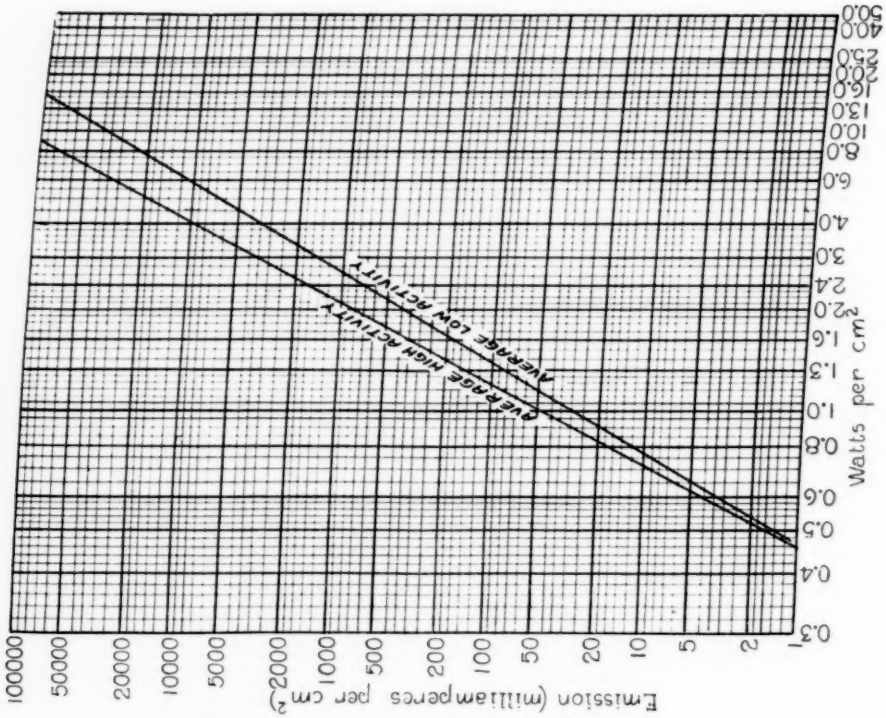
Emission (milliamperes per cm²)
Watts per cm²
AVERAGE HIGH ACTIVITY
AVERAGE LOW ACTIVITY

Fig. 3.

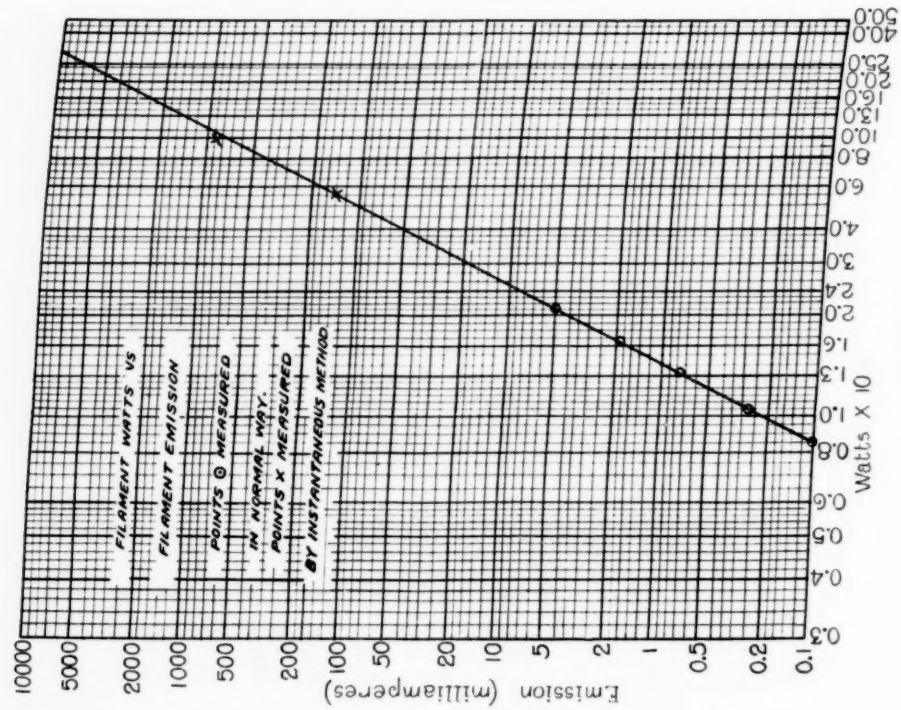
FILAMENT WATTS VS
FILAMENT EMISSION
POINTS ⊙ MEASURED
IN NORMAL WAY.
POINTS × MEASURED
BY INSTANTANEOUS METHOD
Emission (milliamperes)
Watts X 10

Fig. 2.

cm² degree². The values of work function ϕ_0 corresponding to the above values of b_0 are 0.75 volt and 0.905 volt.

A great deal of the work in connection with these measurements was performed by Mr. T. T. Eaton, and to him should go the credit for first noticing the very high efficiencies here reported.

B. J. THOMSON
Vacuum Tube Engineering Department,
General Electric Co.,
September 24, 1930.

Negative Ions in Hydrogen and Water Vapor

In the course of the writer's[1] investigation of the positive ions produced in hydrogen by electron impact the presence of negative ions was observed. These were indicated by the appearance of two sharp peaks when the negative ion current was studied as a function of the electron velocity. They were suspected of being H^- ions and Bleakney upon re-examining hydrogen in his mass spectrograph[2] observed the ions and found them to have the e/m value of H^-. The maxima of the peaks, corresponding to the maxima for the efficiency of their production occurred at electron velocities of 6.6 and 8.8 volts. These negative ions were found to possess kinetic energy, presumably acquired in the dissociation process which accompanies their formation. The velocity of the ions of the 6.6-volt group was about 1.5 volts while that of the 8.8-volt group could not be accurately determined because there were so few of them.

The negative ions were so few in number that it was thought they might be due to an impurity in the hydrogen—most probably water vapor. They persisted, however, after all reasonable precautions were taken to eliminate possible sources of the vapor. On the other hand when water vapor was admitted to the tube and the hydrogen removed the same H^- ions appeared in much greater abundance, and a determination of their velocities could be made.

A preliminary study of their kinetic energies showed that the velocity of the 6.6-volt group was about 1.5 volts while that of the 8.8-volt group was about 3.2 volts. This would mean that if they are formed by dissociation of H_2O^- the energy of the dissociated system is in the first case 5.1 volts above the normal H_2O state and in the second case 5.6 volts.

Bleakney has informed me that he has obtained H^+ ions from H_2O at a minimum electron velocity of 19.2 volts. If we assume that these ions result from the dissociation of H_2O^+ into $H^+ + OH$, we find, by adding an electron to the H^+ that the energy of the system $H + OH$ is 5.7 volts above the normal H_2O state. Less than this by the electron affinity of the H atom would be the energy of the system $H^- + OH$. Assuming that this is the system which results from the 6.6-volt electron impact we find the value 0.6 volts for the electron affinity of the hydrogen atom. It is interesting to note that Hylleraas[3] gives 0.7 volts for this quantity.

The second group of H^- ions appearing at 8.8 volts may possibly result from the dissociation of H_2O^- into H^-, excited, and OH. The energy of this system would be expected to lie above the energy of $H^- + OH$ by the amount of the excitation potential of H^- which would be in the neighborhood of 0.6 volts. (H^- would be expected to resemble He with an excitation potential near its ionization potential.) Actually its energy is 0.5 volts above the energy of the system resulting from the 6.6 volt impacts.

On the other hand if it be true that the H^- ions are formed by dissociation of H_2^- the energy of the system resulting from the 6.6-volt impacts would lie 3.6 volts above the normal state of the H_2 molecule and that resulting from the 8.8-volt impacts 2.4 volts above. The former might be regarded as the heat of dissociation of H_2 less the electron affinity which would give 0.8 volts for the affinity. There is no reasonable explanation of the energy of the state resulting from the 8.8-volt impacts.

Upon combining with thermochemical data the known heats of dissociation of H_2 and O_2 there is obtained

$$H + H + O \rightarrow H_2O + 10.0 \text{ volts.}$$

From the above consideration that $H + OH$ lies 5.7 volts above the normal state of H_2O we see that the heat of dissociation of the OH molecule would be 4.3 volts. The writer has been unable to find any data concerning this.

[1] See paper in this issue.

[2] W. Bleakney, Phys. Rev. **34,** 157 (1929); and Phys. Rev. **35,** 139 (1930).

[3] E. A. Hylleraas, Zeits. f. Physik **63,** 291 (1930).

In conclusion I believe in the reality of the transition

$$H_2O+e\rightarrow H_2O^-\rightarrow H^-+OH$$

but am not certain of the transition

$$H_2+e\rightarrow H_2^-\rightarrow H^-+H.$$

It is hoped that more precise measurements in the future will throw additional light on the matter.

One interesting feature of the phenomena is the extremely narrow range of electron velocities which are capable of producing these negative ions. The range is but little wider than the normal velocity distribution in the electron beam, as though the electrons, to produce a negative ion of a given type, were compelled to have a perfectly precise velocity.

W. WALLACE LOZIER

University of Minnesota
October 6, 1930

Wave Mechanics of Deflected Electrons

In a letter[1] appearing in the September 1 number of the Physical Review, Carl Eckart makes the assertion that the major conclusion of my paper[2] on the above subject is incorrect, and that the difference between $(e/m)_{\text{defl}}$ and $(e/m)_{\text{sp}}$ cannot be explained as a difference between wave and classical mechanics. He attributes the alleged error in my conclusion to the interpolation method of calculating the mean radius of curvature, admitting that the rest of the analysis is correct.

I had not neglected to verify the interpolation formula in question by direct calculation of the mean radius of curvature for the states $k=0$ and $k=1$. Shortly after seeing Dr. Eckart's letter, however, I noticed that the method of interpolation which I had employed is unnecessary, since the mean radius of curvature may be calculated rigorously from Eq. (43) of my paper. This equation does not lead to an infinite series even when p is fractional since k is a positive integer. For the mean radius of curvature it gives

$$\bar{\rho} = \frac{(\pi/2)^{1/2}}{s!}\left[\left(s-\frac{1}{2}\right)!\left(2s+\frac{1}{2}-k\right) + \frac{(s-3/2)!k(2s-\frac{1}{2}-k)}{2^2[1!]^2} + \frac{(s-5/2)!k(k-1)(10s-3/2-9k)}{2^4[2!]^2} + \cdots\right].$$

For the first order correction we need only the first two terms. Using S and K as defined in my paper

$$\bar{\rho} = \left(\frac{\pi}{2}\right)^{1/2}\frac{(s-\frac{1}{2})!}{s!}S\left[1-\frac{K+1}{4S}\right],$$

and applying Stirling's formula

$$\bar{\rho} = S^{1/2}\left[1-\frac{K-1}{4S}\right],$$

which is (except for the negligible -1 in the numerator of the second term) the same formula as obtained by interpolation. Therefore it is clear that Dr. Eckart was mistaken in his assertion that I had been led to incorrect results by the method of interpolation used.

Dr. Eckart bases his criticism of my work on a supposed disagreement between my conclusions and those obtained by Kennard[3] in an earlier paper. Working with the transformation theory of Dirac and Jordan, Kennard obtains the coordinates of the center of a wave packet moving in a magnetic field in terms of initial coordinates and momenta and notices that he is led to a formula identical with that given by classical electrodynamics. He does not, however, obtain the radius of curvature in terms of the energy, which is the significant relation from the experimental point of view. Therefore there does not seem to be any necessary conflict between Kennard's conclusions and mine.

LEIGH PAGE

Yale University
New Haven, Conn.
October 3, 1930

[1] Carl Eckart, Phys. Rev. **36**, 1014 (1930).
[2] Leigh Page, Phys. Rev. **36**, 444 (1930).
[3] E. H. Kennard, Zeits. f. Physik **44**, 347 (1927).

BOOK REVIEWS

Astronomy, An Introduction. ROBERT H. BAKER. Pp. xii+521. D. Van Nostrand Company, Inc., New York: 1930. $3.75.

A few years ago those who were teaching introductory courses in Astronomy in colleges felt the need of a new text. Young's "Manual of Astronomy" and Moulton's "Introduction to Astronomy" were extensively used and both of these books left much to be desired. The science had made such rapid progress since these texts were written that many new discoveries and theories were lacking altogether. With the introduction of "Astronomy" by Professor Baker there are at least five texts from which teachers of beginning courses in Astronomy may choose. The ranges of material presented and the matter of treatment is such that from one of the five texts a satisfactory selection can be made to suit the varying conditions found in different universities and colleges. Without exception the authors have avoided a mathematical presentation of the subject and have endeavored to set forth the fundamental facts and principles of the science with as few mathematical formulas as possible. They have kept in mind the fact that those who are reading the text have studied mathematics no further than trigonometry and have had, in high school or college, only an elementary course in physics. In many instances the authors have been a bit too cautious in the matter of avoiding mathematics. From the writer's own experience a mathematical formula now and then is a good thing even in a "non-mathematical" course. A few formulas sometimes bring a definiteness that satisfies the student and which, were the point in question explained in words, would have a vagueness, that is to say the least, undesirable. Most of the authors have had in mind a text that could be used in a three hour course extending through the college year and which by so doing will meet the requirements of most colleges and universities offering a course in Astronomy as one of the electives in the science group.

"Astronomy, An Introduction" by Doctor Robert H. Baker, Professor of Astronomy in the University of Illinois, is a text that will be found to be highly satisfactory from many points of view. To say that it is up-to-date in the presentation of new material is to cite only one of its merits. The text is printed with excellent type on good paper. It is well bound and illustrated in a manner worthy of the highest praise. Five hundred illustrations and drawings have been included which give added interest and which help in the explanation of the subject matter. The illustrative material is so designated that the chapter and paragraph with which each is associated is indicated. The decimal system has been used throughout. The number to the left of the decimal point indicating the number of the chapter, and the number to the right, the paragraph in the chapter. At the end of each division a list of references is given. These references have been carefully chosen and they form an admirable basis for an up-to-date astronomical library. Such a list of books, periodicals and charts should be available to every college student studying the subject.

The text begins with a chapter on "Aspects of the Sky." The student is introduced at this point to the coordinate systems and to many of the technical terms he will need in understanding the subject. A paragraph is included on "Learning the Constellations" and a few charts are given with directions as to how the constellations may be located in the sky. While this attempt is inadequate it is admittedly a difficult feature to include in a text. It is a mistake to place too much emphasis on the study of the constellations, but a knowledge of the principal configurations should be a part of the stock-in-trade of every student who studies astronomy, and this feature should not be omitted nor neglected. The problems of practical astronomy have been eliminated almost entirely and the relation of geology to astronomy is mentioned only in the briefest manner. More attention is given to a study of the earth's atmosphere and its astronomical effects than is usually found in most texts. The subject of celestial mechanics is dealt with in a concise but adequate manner. The author has succeeded in presenting this material in an interesting way even for one who does not have a special interest for this part of the subject. Of the twelve chapters one is devoted to the sun and five to the siderial system.

This seems to be about a proper division of the material. The latter half of the text calls forth special commendation. In general controversial points are free from bias and new theories are put forth in a manner which in most cases will leave the student with the impression that these theories are only theories and not established facts. The last three chapters deal with The Constellation of the Stars, The Galactic System, and Exterior Galaxies. These chapters will be of interest to general readers who have not been able to keep abreast with recent astronomical literature. With these chapters a climax is reached. It is apparent that Astronomy is an old, yet new, science, that the frontiers offer thrilling adventure and that "What we know compared with what we do not know is immense."

On the whole the book is comparatively free from typographical errors and those, such as they are, will doubtless be eliminated in future printings. In places the mode of expression used by the author may startle the more conservative. Doubtless many will feel that this or that section could have been expanded to advantage. However it is an excellent text which will be welcomed by many who are teaching an introductory course in astronomy.

CLIFFORD C. CRUMP

Electron Physics. J. BARTON HOAG. Pp. 208. D. Van Nostrand Co., Inc., New York, 1930. Price $3.00.

This book is more than a laboratory manual in that the larger part of it is devoted to the descriptions of the physical phenomena which are to be studied rather than to the description of the apparatus used in the experiments. Each chapter describes the fundamentals of a particular topic and concludes with directions for performing one or more experiments. These are designed to acquaint the student with the technique used in that field and to obtain an understanding of the subject such as is afforded by a good laboratory experiment. The discussion usually includes a number of different experiments which may be performed, but detailed procedures are given for only one or two of the possible experiments, selecting those which are best adapted to the use of simple apparatus and which will yield satisfactory results in the hands of the student. For example, in the chapter on "The Electron" the determination of $N.e$ by electrolysis, the determination of N from Brownian movements and from the recent measurements of x-ray wave-lengths by means of ruled gratings are given. Also the cloud expansion method, the balanced oil drop, and the shot effect methods of measuring e are described but detailed directions are given for the student to measure e by the oil drop method only.

There is given a number of experiments which may well displace some of those experiments which have become "classical" in the intermediate laboratory courses or which may be added to that group if time permits. For example, the test of Richardson's emission equation, the measurement of the thermionic work function, the characteristics of the photoelectric cell and of the three-electrode tube, measurement of ionization potentials and the absorption of x-rays are experiments well worth the attention of the student of modern physics. The book also gives a number of experiments in radioactivity.

Appendices on electrometers, electroscopes, pressure gauges, vacuum technique and the production of vacua, also a number of tables add to the value of the book. References at the end of each chapter and a group of numerical problems with answers are given.

J. W. BUCHTA